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ABSTRACTS
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THE AMERICAN CERAMIC SOCIETY

2525 North High St. Columbus, Ohio

THE CONSTITUTION OF GLASS*

By George W. Morey

ABSTRACT

Glass is to be regarded as a liquid which has a viscosity so great as to be practically rigid; and the glasses of commerce are all solutions undercooled far below their normal crystallizing temperatures. Nothing more is known regarding the constitution of these highly concentrated solutions than is known about the constitution of other concentrated solutions. The phase-equilibrium diagram gives no information as to the compounds present in the liquid phase, for there is no known correlation between the properties of a homogeneous system and those of the heterogeneous system formed from it on crystallization. Evidence based on the rate of volatilization of alkali from alkali-silicate glasses does not indicate compound formation. The discontinuous change of properties of a glass in the "annealing range" has been considered by some to be evidence that the glassy state is a fourth state of matter separated from the liquid state by this transition temperature; by others, as indicating that above this discontinuity the material is a liquid, below it, a brittle solid. These views are unsound, because they are based on measurements of physical properties made with changing temperature when those properties themselves not only change with temperature but also require at each temperature considerable time to reach their equilibrium value. When the measurements are made on glasses which have been held at constant temperature long enough for the equilibrium value of the property to be attained, no discontinuities are observed and there is no justification for calling glass a fourth state of matter or for separating a "brittle" from a "viscous" temperature range. Arguments, based on the variation of physical properties with composition in which it is considered that such variation is represented not by a continuous curve but by a series of straight lines determined by the composition of hypothetical compounds, are shown to be theoretically improbable and not in accord with the facts. Recent speculations on the constitution of glass based on X-ray evidence and recent studies of glass by means of X-rays indicate that the glassy state is distinguished by a random nonrepeating atomic network. This conclusion is in harmony with the view that glass is an undercooled liquid representing a solution in which definite compounds can not be identified.

I. Introduction

The problem of the constitution of glass has been discussed by many writers, but there is no unanimity of opinion on the subject. That such is the case is not surprising. When one speaks of the constitution of glass, there is an implication of a knowledge far more profound than is expressed by a chemical analysis, a knowledge extending to details of the atomic and molecular arrangement concerning which we have no information and no method of obtaining information.

(1) Constitution of Gases The molecular hypothesis of Avogadro and the law of the equipartition of energy give positive information as to the molecular species present in a gas, whether it be one of the inert gases, a monatomic gas, a diatomic or a triatomic gas, or an equilibrium mixture of more than one molecular species, such as nitrogen dioxide.

(2) Constitution of Crystals We also have knowledge of the constitution of crystals, thanks to the insight into their structure given by X-rays. In the simpler crystals we can with fair precision fix the position of every atom, and there is no doubt that the structure of many compounds crystallizing in the cubic system has been uniquely determined. Unique structures of more complicated crystals are not so readily obtained, and many of the structures which have been proposed for silicates rest in part on X-ray evidence, in part on hypotheses concerning the arrangement of the oxygen atoms which lack experimental verification. Nevertheless, we do have a real knowledge of the constitution of some crystals and have made highly probable deductions in regard to others, including many silicates.

(3) Constitution of Liquids But when we come to liquids we are forced to admit that we know but little about their constitution, if by constitution we mean the inter-relations of the various atoms and molecules to each other. To be sure, in a comparatively large number of liquids of a nonpolar type, such as benzene, we may make the highly plausible assumption that the structure is that of a completely heterogeneous assemblage of simple molecules corresponding to the chemical formula and that their thermodynamic properties are in harmony with this assumption. But this does not prove that the assumption is correct, because the data are not competent either to prove or disprove.

Liquids of a different type, such as water, require further assumptions to explain their proper-

* Presented at the Annual Meeting, American Ceramic Society, Cincinnati, Ohio, February, 1934 (Glass Division). Received March 15, 1934.

ties. The varying density of water, with a maximum at 4°, is unexplainable without the aid of hypotheses regarding the constitution of water; and it is generally admitted that such property-temperature curves can be accounted for by the presence in water of three different molecular species. But this does not prove the existence of such species; we have a complicated curve which can only be fitted by putting into our equations several variables, and when our equations fit the facts we are merely good mathematicians. At present the whole theory of molecular association in pure liquids is in an unsettled condition. Older concepts, such as that relating molecular association with the variation in free surface energy, as embodied in the rule of Eötvos, Ramsay, and Shields, are thoroughly discredited, but as yet the newer methods of quantum mechanics have not provided a concept of the molecular arrangement in liquids of the "associated" type. In this connection a suggestive paper is that of Bernal and Fowler,[1] which appears to offer a picture of the structure of liquid water which is in harmony both with modern physical theory and with chemical facts.

(4) Constitution of Solutions Meager as is our knowledge of pure liquids, still more meager is our knowledge of solutions. It was early observed by Raoult that in the case of certain liquids, which we now call nonpolar, the change in thermodynamic properties with composition followed a simple law, which was not even approximately followed by other solutions, especially salts in water. Then van't Hoff and Arrhenius introduced the dissociation theory according to which solutions which do not obey Raoult's law are made to obey it by multiplying the salt concentration by a factor called the degree of dissociation. This fruitful hypothesis has been the inspiration of much experimental work and has served to correlate a multitude of experimental facts; but in its quantitative application it has not been so happy. The simple dilution law of Ostwald is applicable only in solutions too dilute to be of general interest; and all the modifications of it, up to the Debye-Hueckel hypotheses, have been of more value for mathematical recreation than for explaining the properties of real solutions.

In spite of the labors of three generations, we still lack a theory of concentrated solutions; we can not yet speak with assurance of the constitution of an aqueous solution of common salt. But glasses are highly concentrated solutions, and it is not surprising that the clue to their constitution is lacking. Indeed, it is not unreasonable to hope that the clue to the whole problem of concentrated solutions may come from glasses, as these very convenient solutions can be studied over a wide range of temperature, from the region in which they are unsaturated, through the region in which they become saturated with respect to one, two, or three several phases. At present our knowledge of the variation of physical properties with composition in glass-forming systems is more extensive and complete than in any other type of solution.

II. Physical Properties of Glasses at Different Temperatures

The physical properties of glasses which have been determined over a temperature range exceeding 1000°C may with advantage be discussed in three categories, which may roughly be termed the high temperature region above the annealing range, the annealing range itself, and temperatures below the annealing range. It will not make the annealing range too specific if we define it as the interval for a particular glass below the temperature at which strain as observed by optical means disappears practically instantaneously and above the temperature at which no permanent strain results when the glass is quickly chilled. First consider the high-temperature region.

(1) Properties at High Temperatures The properties to be considered at high temperatures are of two sorts, namely, physical properties of liquids as functions of temperature and composition, and devitrification, which puts an end to the existence of liquid and ruins the glass. Indeed, that property of glass which makes possible its manufacture and working, namely, the property of remaining in the noncrystallized condition while passing through the temperature range immediately below that at which crystals should begin to form and persisting in that condition indefinitely at ordinary temperature, is the most important and characteristic property of glass. The temperature at which there is equilibrium between the first trace of a crystalline phase and the liquid is known as the liquidus temperature and is the

[1] J. D. Bernal and R. H. Fowler, *Jour. Chem. Phys.*, **1**, 515 (1933).

most important constant in connection with the devitrification of glass. Not only does the liquidus temperature change with composition, but also the identity of the first crystalline phase to separate changes, and the entire composition diagram may be subdivided into fields, each of which is characterized by a different primary phase. The liquidus temperatures for several glass-forming systems have been determined, but the chief feature of interest at present is the fact that such diagrams show that the compounds which separate as primary phases from the best glasses are characterized either by decomposing before their melting points are reached or by flat melting-point curves.

In the hypothetical case in which a compound melts without dissociation, that is, to a liquid containing no representatives of any molecular species other than those which give rise to the crystalline compound, addition of either of the components of the compound will result in a sharp lowering of the melting point, and the two freezing-point curves will intersect at an angle at the composition of the compound. Since there is no dissociation, addition of either component will add a new molecular species to the liquid, and the resulting freezing-point depression will be the same as if some other substance, not a constituent of the compound, had been added. If, on the other hand, dissociation takes place, there will be in the liquid, formed by melting the pure compound, representatives of the same molecular species as are obtained on adding excess of either component, and the melting-point curve will be flat and will have a horizontal tangent at the composition of the compound. Silicates as a whole, and especially all of the alkali and alkaline earth silicates with fields near the composition of common glass, are characterized either by incongruent melting points, or by unusually flat melting-point curves, both indicative of much dissociation, and it follows that in the glass there exists but a small proportion of these compounds. The compound which freezes out on cooling is not necessarily that which is present in greatest amount in the liquid. It is a question of solubility, and that compound whose solubility limit is first reached will be the first to crystallize. In the liquid there will be an equilibrium between the various molecular species, and when one of these is removed by precipitation, reactions will take place with formation of that compound whose concentration has been diminished by its freezing out.

In discussing the problem of the constitution of glass, it is natural to use such expressions as have been used above, "compounds in the liquid" and "molecular species," but it is not easy to attach any definite meaning to such expressions. There can be no doubt that compounds do exist in the liquid. Probably no one would urge that all of the components are present as oxides in mutual "perfect" solution. There undoubtedly is a large amount of combination of these oxides into molecular groupings or compounds, but these groupings probably are not static but dynamic. "Combination" between the various atoms and atomic groupings results from a more or less complete interlocking of the various fields of force. The haphazard atomic arrangement of a liquid makes improbable the complete saturation of the fields of force in any one-to-one atomic grouping, but indicates rather a sharing of the atomic binding forces over several adjacent atoms. Such diffuse linkages will give rise to representatives of every possible atomic arrangement and will show a preponderance of those atomic associations which most completely satisfy the potential requirements, but it is doubtful if any more definite picture of compound formation is justifiable. Nor is it helpful to speak of "solvation." That merely brings in a new technical term, whose meaning in this connection is hazy and indefinite. Solvation consists in the association of molecules or ions of the solution with molecules of the solvent. It is idle to distinguish only one component of a glassy melt as solvent. The word has a meaning only when one constituent is present in preponderant excess, as in a solution of KNO_3 in H_2O at ordinary temperatures. But when that solution is considered near the melting point of KNO_3, where the liquid contains but a small proportion of H_2O, the distinction between solvent and solute has disappeared, as has also any artificial distinction between the processes of solution and fusion. Solvation is a descriptive term suggestive of a loose type of chemical combination. But the only type of combination we can logically assume in a complex liquid whose components form dissociating compounds is loose and dynamic, a statistical preponderance of certain molecular types. The proportions of the various possible types will vary with temperature and in a continuous manner, but we are unable to

identify these types or to differentiate the various ways of regarding them. Solvation, molecular aggregation, molecular equilibrium are, from a pragmatic standpoint, merely words indicating that something, we know not what, is going on in the solution.

The most probable condition at high temperature of a silicate mixture such as glass may be that of a solution containing representatives of all possible "molecular species," in proportions dependent upon the composition and the temperature, and changing with decreasing temperature in the direction of increasing proportion of the more complex molecular species. The high melting points of the orthosilicate compounds and their stability at high temperatures make it probable that they constitute a large proportion of the molecular species even in trisilicate glasses; and the extensive dissociation of the more complex silicates such as $Na_2O{\cdot}3CaO{\cdot}6SiO_2$ makes it probable that they exist in much smaller amount than corresponds to stoichiometrical proportions. But the very existence in the liquid of molecules such as $Na_2O{\cdot}3CaO{\cdot}6SiO_2$ is entirely hypothetical. That such a compound exists in the crystalline state is undoubted; but a crystal is a definite three-dimensional structural identity, and to identify the unknown molecular agglomeration which on crystallizing becomes that compound, if any such exist, as having the composition of the crystalline compound is an extrapolation of our knowledge which, however plausible, is unwarranted. The existence of certain compounds as the stable products of crystallization of a liquid is no evidence that they exist as such in the liquid, and no knowledge we have at present permits the identification of any compounds existing in the liquid state.

Attempts to discover the compounds present in glass, either as such at ordinary temperatures or in the far less viscous liquid which it becomes on heating, usually take the form of finding departures from a linear relation between composition and some property of the glass. This procedure is based on the hypothesis that the properties in question, specific volume, refractivity, surface tension, and viscosity, are linear functions of composition when no combination takes place between the components; and that when such combination takes place the properties become linear functions not of the components themselves but of the compounds formed between them. Such an assumption was long ago discarded[2] as untenable for those aqueous solutions which have been most widely studied. Nevertheless, it is resurrected again and again, sometimes for one property of solutions, sometimes for another. For example, Tammann,[3] from the extensive study which has been made of the properties of H_2O–SO_3 mixtures, concluded that the viscosity is the only property which indicates in the liquid the presence of compounds known from the freezing-point curves. Later,[4] in a study of all available data from other systems, he finds 8 cases in which compounds are indicated by maxima on both the viscosity curve and the freezing-point curve; 2 cases in which one compound is indicated by viscosity data, but other compounds in the same system are not indicated; 11 cases in which the maximum is at a different composition from that of the compound; 17 cases in which there is a maximum in the viscosity curve, but no compound; 6 cases in which the viscosity curve has no maximum, but lies above the line joining the viscosity of the two components, and a compound is shown by the freezing-point curve; 3 cases in which the continuous viscosity curve lies below the line joining the viscosities of the two components, and a compound is known; and 7 cases in which there is a maximum on the viscosity curve, but the melting-point curve shows only a eutectic. Still later[5] he finds a case in which there is a minimum on the viscosity curve at the composition of the compound. Evidently the viscosity is a frail reed on which to base an argument as to the existence of compounds in a liquid phase.

In spite of the accumulation of an enormous amount of data, we have not yet any intimation of a hypothesis which will enable us to predict the heterogeneous equilibrium from the properties of a homogeneous equilibrium. To be sure, by applying laws of so-called ideal solutions to exceptional binary mixtures the freezing-point curves of the two components can be calculated

[2] See the controversy arising out of Mendeléeff's "theory of solutions," based on the inference of the existence of water-soluble compounds from the density curve of the binary mixtures. D. Mendeléeff, *Jour. Chem. Soc.*, **51**, 778 (1887); S. U. Pickering, *ibid.*, **57**, 64, 331 (1890); *Phil. Mag.* **29** [5], 427 (1890); Watt's Dict. Chem., art. "Solutions" ii (1894); H. Crompton, *Jour. Chem. Soc.*, **53**, 116 (1888); S. Arrhenius, *Phil. Mag.* **28** [5], 36 (1889); E. H. Hayes, *ibid.* **32** [5], 99 (1891); A. W. Rücker, *ibid.* **32** [5], 306 (1891); S. Lupton, *ibid.*, **31** [5], 418 (1891).

[3] G. Tammann, *Z. anorg. allgem. Chem.*, **161**, 363 (1927).

[4] *Ibid.*, **172**, 242 (1928).

[5] *Ibid.*, **199**, 117 (1933).

to a reasonable degree of approximation, and from their intersection the eutectic composition and temperature obtained. But in the great majority of cases, without exception in all cases resembling silicate mixtures, such a calculation is not approximately fulfilled. In no case have we any intimation as to why a compound is formed.

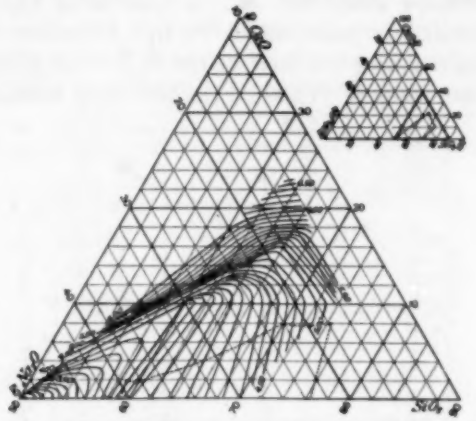

FIG. 1.—Log isokoms (lines of constant viscosity) in the system, Na_2O–CaO–SiO_2, at 900°. Viscosity in log poises; composition in weight per cent. The broken line is the liquidus curve at 900°.

From no theoretical knowledge available today could one predict that a compound of the composition $K_2O \cdot 4SiO_2$ will be formed in the system, K_2O–SiO_2, and no similar compound in the system, Na_2O–SiO_2; or that lithium disilicate will have an incongruent melting point while sodium and potassium disilicates have congruent melting points. The prediction of the heterogeneous equilibrium from the properties of the components of the homogeneous equilibrium, a fundamental objective of theoretical chemistry, is far from our capabilities at the present time, and there is no known relationship between the properties of a solution and of the substances which form from it on completion of the process of crystallization.

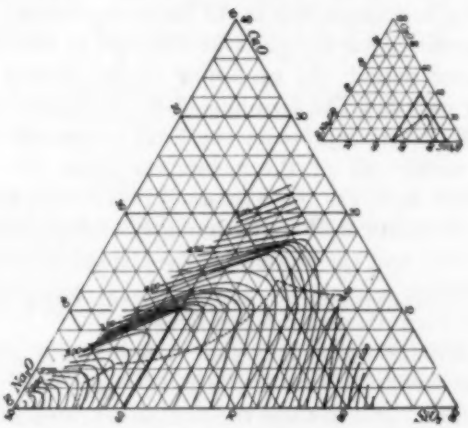

FIG. 2.—Log isokoms (lines of constant viscosity) in the system, Na_2O–CaO–SiO_2, at 1000°. Viscosity in log poises; composition in weight per cent. The broken line is the liquidus curve at 1000°.

The lack of correlation between the properties of the liquid at high temperature and the phase-equilibrium diagram is well illustrated by Figs. 1, 2, and 3, in which are represented the lines of equal viscosity in the system, Na_2O–CaO–SiO_2, at various temperatures, as determined by Washburn, Shelton, and Libman,[6] together with the boundaries of the liquid[7] at the same temperature. Within the restricted area formed by the liquid boundaries the liquid alone is stable; outside of this region the melt at equilibrium should consist of crystals and liquid. It is evident that the reactions which should take place, but do not, are without effect on the viscosity.

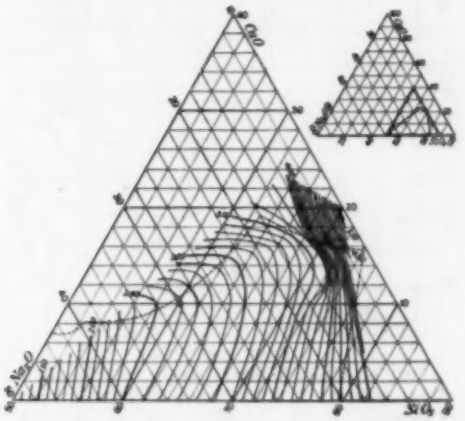

FIG. 3.—Log isokoms (lines of constant viscosity) in the system, Na_2O–CaO–SiO_2, at 1100°. Viscosity in log poises; composition in weight per cent. The broken line is the liquidus curve at 1100°.

Recent work on the vaporization of alkali from an alkali oxide-silica glass[8] has been considered to give evidence as to the existence of compounds in glass. It is stated, "So that, up to as high a temperature as 1400° the molten glasses contain-

[6] E. W. Washburn, G. R. Shelton, and E. E. Libman, *Univ. of Ill. Bull.*, No. 140 (1924).

[7] G. W. Morey and N. L. Bowen, *Jour. Soc. Glass Tech.*, 9, 226 (1925).

[8] (*a*) E. Preston and W. E. S. Turner, "Alkali-Lead Oxide-Silica Glasses," *Jour. Soc. Glass Tech.*, **16**, 219 (1932).
(*b*) Eric Preston and W. E. S. Turner, "Sodium-Silicate Glasses," *ibid.*, **16**, 330 (1933).
(*c*) E. Preston and W. E. S. Turner, "Potassium Oxide-Silica Glasses," *ibid.*, **17**, 122 (1933).

ing sodium oxide and silica appear to consist of a mixture of silicates, or of a silicate with the constituent in excess, the silicates existing with but little dissociation." Again, ". . ..all the evidence points to the existence, in the fused soda-silica glasses, of sodium metasilicate and sodium disilicate, when the Na_2O content is greater than 34%, and to sodium disilicate and silica in glasses containing less than this amount." These conclusions are so important that it is desirable to scrutinize carefully the evidence put forward to

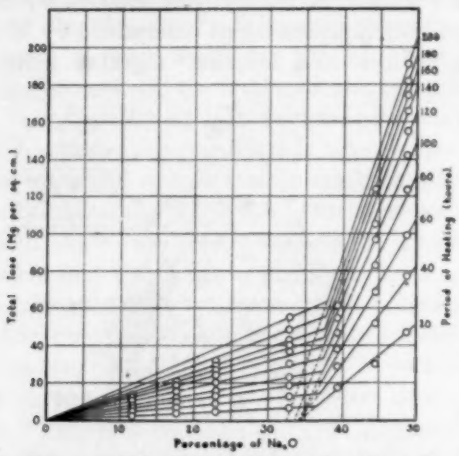

FIG. 4.—Volatilization losses for the soda-silica glasses at 1400° (after Preston and Turner).

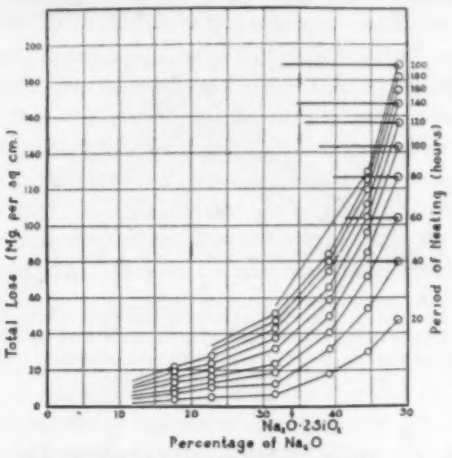

FIG. 5.—Volatilization losses for the soda-silica glasses at 1400° (redrawn from Preston and Turner).

sustain them. Only the second paper enumerated, from which the quotations are taken, will be discussed. The conclusions reached in it are more sweeping than in either of the other papers, and criticisms similar to those given for the second paper are applicable to the other two.[9]

An important part of the argument is based on Fig. 4, which gives the total loss by volatilization, in milligrams per square centimeter, plotted as a function of the time, for seven glasses whose initial composition is represented by the vertical sequence of points. As drawn, the families of curves are striking; but there is much arbitrariness in the way they are drawn. The author has replotted them in Fig. 5, connecting the various points for the same duration of heating by straight lines, merely to present the most unbiased picture of the results. To the writer it seems that to represent the last three points on each curve by straight lines intersecting the zero axis at the composition of sodium disilicate is without justification, but that is not the major criticism of this figure. It represents the total loss per unit area at successive intervals of time of glasses of the initial composition indicated; but the change in composition of the glasses is not a negligible amount. For the first glass on the right-hand side, No. 114, a horizontal line is drawn at each point, indicating by its terminus the composition of the melt at the beginning of that 20-hour period. That is, the left-hand terminus of the horizontal line at 40 hours represents the composition of the glass at the end of the first 20-hour period, the beginning of the second 20-hour period. The terminus of the horizontal line at 200 hours represents the final composition of the melt. All of the points for glass 114 are plotted as if the glass retained that composition, but in reality it is of continuously changing composition, and the amount of the change is such as to vitiate completely all the conclusions which have been drawn from this figure.

Another argument is that the curves of Fig. 6 (Preston and Turner's Fig. 7) fall into two families. But in these the ordinates represent the quantity, $\log \cdot \left[\frac{A - 2x}{A}\right]$, the values of which have been calculated in different ways for the two groups of glasses. In the one group, A represents the weight per cent Na_2O in a mixture of Na_2O and SiO_2; in the other, the percentage of sodium metasilicate in a mixture of sodium metasilicate and sodium disilicate. They fall into two groups because they are calculated on a different basis,

[9] E. Preston and W. E. S. Turner, *Jour. Amer. Ceram. Soc.*, **17** [2], 26 (1934), discuss the constitution of glass and come to conclusions similar to those contained herein, with the exception of the work by them under discussion.

but when both are calculated on the same basis (Fig. 7), the weight per cent of Na_2O, a separation into two groups seems no longer to exist.

It is evident that the conclusions quoted are not justified by the experimental results on which they are founded, but even more can be said. While we can not make the categorical statement that in a system such as this there can be no discontinuities in such properties as the specific volume or the viscosity, we can be assured that the vapor pressure of any component from such a

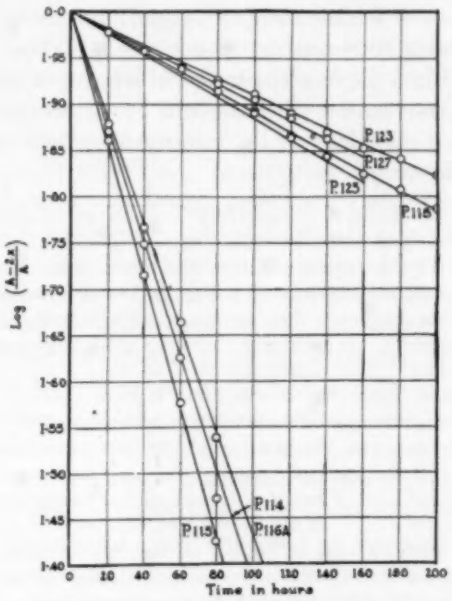

FIG. 6.—Effect of time on volatilization from the soda-silica glasses (after Preston and Turner).

continuous series of liquids can not be a discontinuous, but must be a continuous function of the composition.

III. Properties at Annealing Temperatures

The various theories of the constitution of glass based on studies in and near the "annealing range" are from an entirely different point of view from those at either higher or lower temperatures, and many of them suggest fundamental changes in our views as to the nature of glass. They are based on a large number of observations by many experimenters indicating that when the change of physical properties with temperature is measured in the annealing range a more or less well-marked discontinuity becomes apparent.

The first observation of this type was that of Day and Allen.[10] "On every occasion when borax glass was heated rapidly, either powdered or in the solid block, a slight but persistent absorption of heat appeared in the same region (490 to 500°) and continued over some 20°, after which the original rate of heating returned."

A similar effect was found by So,[11] and later studied extensively by Tool[12] and his colleagues at the Bureau of Standards. Other studies at the Bureau[13] established the fact that the thermal dilatation of glass showed an abnormal increase

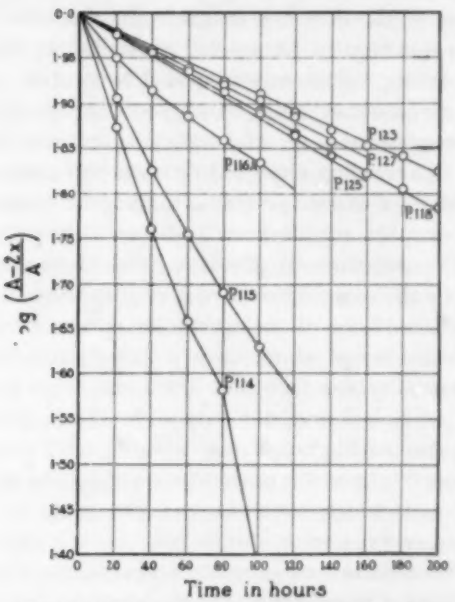

FIG. 7.—Effect of time on volatilization from the soda-silica glasses (redrawn from Preston and Turner).

at the same temperature, and that the properties[14] of glass were altered by variations in the heat treatment in the same temperature region.

Schönborn[15] found that the change with temperature of the electrical resistance of glass could be represented by two straight lines of the

[10] A. L. Day and E. T. Allen, *Carnegie Inst. Washington Pub.*, No. 31, p. 34 (1903).
[11] M. So, *Proc. Tokyo Math. Phys. Sci. Soc.*, **9**, 425 (1918).
[12] A. Q. Tool and C. G. Eichlin, *Jour. Opt. Soc. Amer.*, **4**, 340 (1920); A. Q. Tool and J. Valasek, *Bur. Stand. Sci. Paper*, No. 358 (1920); A. Q. Tool and C. G. Eichlin, *Jour. Amer. Ceram. Soc.*, **14** [4], 276 (1931).
[13] C. G. Peters and C. H. Cragoe, *Jour. Opt. Soc. Amer.*, **4**, 105 (1920).
[14] C. G. Peters, *Bur. Stand. Sci. Paper*, No. 521 (1926); L. W. Tilton, A. N. Finn, and A. Q. Tool, *ibid.*, No. 572 (1923); G. E. Merritt, *Bur. Stand. Jour. Research*, **5**, 627 (1930).
[15] H. Schönborn, *Sprechsaal*, **61**, 99 (1928).

form, $\log W = (A/T) + B$, with an intersection at about the upper limit of the "critical range," as determined by expansivity measurements. Similar results were obtained by Fulda.[16] This intersection was called a "transition temperature." The Society of Glass Technology and the Deutsche Glastechnische Gesellschaft[17] proposed the temperature of this break in the electrical conductivity-temperature curve, determined with a heating rate of 4°C per minute, as a standard method for the specification of the transformation temperature.

One of the first explanations of these observations was that of Lebedeff,[18] according to whose hypothesis, "glass was supposed to contain very minute quartz crystals, which probably contained other substances in solid solution, and the function of annealing appeared to be not so much the removal of stress as the attaining of complete polymorphic equilibrium." Such a hypothesis is of course theoretically untenable, assuming as it does the carrying over of a phase change characteristic of one of the crystalline species of silica into the liquid state, and it is experimentally confuted by the fact that the same type of discontinuity is found, not only with silicate glasses, but also with phosphates, borates, and organic glasses.[19] Indeed it probably is a characteristic of all liquids which have reached a viscosity of 10^{14} poises or greater.

The evidence of several observers, tending to establish a discontinuity in the change of properties of glass with temperature, has been summarized and discussed by Berger, whose interpretation of the experimental data is different from that here proposed. Berger[20] states, "But in a small temperature range, or more exactly, at a temperature point, the temperature coefficients of the properties become discontinuous." "It is noteworthy that in the case of noncrystalline freezing, all property curves break at the transformation point, *Tg*, the temperature coefficients undergoing sudden changes at this point." "The transformation point represents the boundary temperature between viscous and brittle glass, at which boundary the property-temperature coefficients more or less suddenly change." Simon[21] has a similar interpretation, differing mainly in phraseology. He considers that above the transition temperature the material is an undercooled liquid in internal thermodynamic equilibrium; below the transition, a glass, not in internal thermodynamic equilibrium. Both Berger and Simon accept the reality and uniqueness of the transition temperature.

The hypothesis of a transition temperature in glass, above which it is a liquid, below which, a solid or a fourth state of matter, has from the beginning been unacceptable to many. Tool and Hill,[22] in a paper contributed to a Symposium on the Constitution of Glass held by the Society of Glass Technology in 1925, summarize their views as follows:

> ... under proper cooling conditions, certain processes or reactions practically reversible without drastic treatment and involving some or all of the constituent molecules of a glass shall advance in such a way that other possible and disturbing processes often associated with cooling and with treatments at temperatures above the annealing range are prevented. A consideration of the above conclusions indicates that...the condition of a glass...at ordinary temperatures may be considered as undercooled, not alone with regard to the process of crystallization, usually known as the true solidification, but also with respect to the completion of many processes normal to the vitreous condition. .... It has been shown that some of these at least advance and retrogress as the heat treatment is changed and that as a consequence certain properties are modified by altering the effective heat treatment.
>
> The character of the processes and the rate at which they advance will change as the glass cools, and, when it is held at any given temperature, this rate should decrease with time until a state of practical equilibrium becomes established after a period the length of which depends on the temperature. In those ranges in which glass is easily deformable, this period should be relatively short and in the upper part of the annealing range will not exceed an hour, perhaps, but not far below the lower part it may approach a duration of months.

Tool and Hill evidently consider the processes which take place in the annealing range to be continuous. Similar views were expressed by Morey and Bowen[23] in a contribution to the same Symposium. Koerner and Salmang[24] showed by

[16] M. Fulda, *ibid.*, **60**, 769, 789, 810, 831, 853 (1927).
[17] *Jour. Soc. Glass Tech.* [Proc.], **14**, 159 (1930).
[18] A. A. Lebedeff, *Trans. Opt. Inst. Petrograd*, No. 10, p. 2 (1921); *Jour. Soc. Glass Tech.* [Abs.], **6**, 110 (1922).
[19] M. Samsoen, *Compt. rend.*, **182**, 517 (1926); *Jour. Soc. Glass Tech.* [Abs.], **10**, 169 (1926).
[20] E. Berger, *Jour. Amer. Ceram. Soc.*, **15** [12], 647 (1932). In this paper are given references to earlier papers by Berger, and numerous other references.
[21] F. Simon, *Z. anorg. allgem. Chem.*, **203**, 219 (1931).
[22] A. Q. Tool and E. E. Hill, *Jour. Soc. Glass Tech.*, **9**, 185 (1925).
[23] G. W. Morey and N. L. Bowen, *Jour. Soc. Glass Tech.*, **9**, 261 (1925).
[24] O. Koerner and H. Salmang, *Z. anorg. allgem. Chem.*, **199**, 235 (1931).

dilatometric measurements that the position of the transition temperature is dependent on the heating rate, and they consider it solely an undercooling or overheating phenomenon. Annealed glass flows below the transformation temperature.

Further researches have confirmed the view of the continuity of the changes which take place in glass in the annealing range and even to lower temperatures. The discussion by Littleton[25] establishes this in an adequate manner. The evidence of a "change in state" obtained from measurements of thermal expansion, viscosity, and electrical conductivity is critically discussed with the aid of new measurements of the electrical conductivity and the viscosity, and the conclusion is reached that "there are no critical temperatures in the properties of glasses. There is a change of some sort, possibly in degree of dissociation or a molecular aggregation which occurs at all temperatures until a stabilization has taken place." In other words, the properties of glass change with temperature at a rate which is dependent on the temperature. At higher temperatures this change takes place rapidly, so that the properties as measured represent the equilibrium values of those properties at the temperature in question. As the temperature is lowered the rate at which these equilibrium values are reached diminishes, until well below the annealing range it is necessary to hold the glass an impracticable length of time for the equilibrium value to be reached. That even far below the annealing range continuous change does take place has been shown by several observers. Morey and Merwin[26] showed that the attainment of an equilibrium or maximum density required an increasingly long time as the temperature was lowered below the annealing range, but that when the heat treatment was prolonged for several months the glasses did change in density, reaching a value higher than the maximum which would be reached at the ordinary annealing temperature. Lillie[27] showed that in the lower portion of the annealing range several days are required to reach the equilibrium viscosity, which may be approached from either lower or higher temperatures. At temperatures at which the equilibrium value of the viscosity of glass is 3.38×10^{15}, the viscosity in three days had increased from an initial value of 0.2×10^{15} to 2.6×10^{15}, indicating that a considerably longer time would have been required for the glass to reach a state of equilibrium in regard to viscosity. The annealing experiments on Pyrex brand resistant glass, reported by Morey[28] at the February, 1932, Meeting of the American Ceramic Society, at a temperature at which the viscosity of the glass is of the order of 10^{19} poises, were continued until December, 1933, making a total of two years. The rate of decrease of strain remained essentially constant for over twenty-two months of that period, but an initial period of six weeks was required for the glass to assume a constant condition. The conclusion seems inescapable that there is no discontinuity of properties in the annealing range or even well below that range, provided the measurements are made on glasses which have been held at constant temperature long enough for the equilibrium values to be attained. There is no justification for assigning any particular temperature as the boundary line between "viscous" and "brittle" glass, or for a boundary between the "undercooled liquid" and the "amorphous solid" condition. And it should be emphasized that discontinuities, found from measurements made with continuously changing temperature on properties which not only change with temperature but also require considerable time to reach an equilibrium value, can not be admitted as evidence of a real change in the condition of the glass.

Nor is it to be expected that slight changes in the rate of heating will greatly modify such discontinuities. The fact that a discontinuity is observed at all with a continuous heating indicates that a stored-up lag in the glass is suddenly released, and slight modifications in heating rate can but slightly modify the temperature at which the release takes place. The fact that such slight changes in heating rate in the region of high viscosity only slightly modify the temperature of such apparent discontinuities is not evidence of their reality. Experimenters are urged to make their measurements on glasses in an equilibrium condition and to show that such a condition has been reached as was done by Lillie.

The importance of the transition to the crystalline condition should not be overlooked in this discussion. It has been often implied, and some-

[25] J. T. Littleton, *Ind. Eng. Chem.*, **25**, 748 (1933).
[26] G. W. Morey and H. E. Merwin, *Jour. Opt. Soc. Amer.*, **22**, 632 (1932).
[27] H. R. Lillie, *Jour. Amer. Ceram. Soc.*, **16** [12], 619 (1933).
[28] To be published in detail soon.

times stated, that below the transition temperature the glass is solid, molecular movement is impossible, and devitrification can not take place. Berger even affirms that the crystalline phase becomes unstable with respect to the glass at a temperature well below the transition temperature. No evidence is given for this extraordinary view; nevertheless Zwicky[29] has assumed its truth in a discussion of the crystalline state. As a matter of fact, most glasses can without difficulty be crystallized below the transition temperature. Several examples are mentioned incidentally by Morey and Merwin.[30] The writer has crystallized $Na_2O{\cdot}SiO_2$ glass by long heating at 200°. Some glasses, such as those made by rapid cooling of Sb_2O_3 or selenium, will crystallize spontaneously at room temperature, even though they are hard and very brittle glasses. Wietzel,[31] testing the "third law" of thermodynamics for fused and crystalline silica, concluded that the entropy of the fused was greater than that of the crystalline at liquid hydrogen temperatures. Gibson and Giaque[32] found the entropy of glycerine in the condition of an undercooled liquid exceeded that in the crystalline condition by 5.6 calories per degree per mole at 70°K. There is no evidence in support of the improbable hypothesis that at lower temperatures the glassy form becomes more stable than the crystalline, and abundant evidence exists and can readily be confirmed that devitrification may take place far below the so-called transition temperature.

IV. Properties below Annealing Temperatures

Two methods have been applied to the elucidation of the constitution of glass at ordinary temperatures. In any such study it must be remembered that the glass represents a rigid material which has cooled with continuously increasing viscosity from above its crystallizing temperature, first through a region in which its properties quickly take on the values characteristic of equilibrium, then through a region in which an increasingly long time is required for the equilibrium to be reached, so that, even though the glass may have been "annealed," its properties at ordinary temperatures represent the frozen-in equilibrium corresponding to some, usually unknown, higher temperature. If glasses are to be compared, they should be in some comparable state, but what that state should be is unknown. It has been shown by many authors that the properties of the cooled glasses are dependent on their thermal history, and it is not sufficient merely to anneal to remove mechanical strain. Such strain does exist in glass quickly cooled, but, as Adams[33] has shown, it can have no effect on density and presumably not on such other properties as refractive index or electrical conductivity. The real differences that are found are the result of differences in heat treatment, and many of the differences between the results of recent observers are to be ascribed to differences in heat treatment adopted by them. But we have no reason for saying that any one of these treatments is erroneous or that any other is the correct one. Such categorical statements must wait until we know what are the fundamental reasons for the effects observed and then what is the comparable condition at which we should aim.

Many experimenters have considered that the presence of compounds in glass at ordinary temperatures could be shown by discontinuities in the property-composition curves. The specific volume is the favorite property for the support of these speculations, with refractive index or specific refractivity the second choice. The validity of the fundamental assumption underlying this treatment has already been discussed and, whether or not the conclusions reached appear valid, it must be admitted that for deviation from linear relationship between composition and property to be proof of compound formation it is necessary that the data be unexceptionable and susceptible of no other interpretation. We do not require that the proof be necessary and sufficient, since that is a desideratum rarely attained in physical chemistry, but we should require that the experimental results be adequate, both in number and precision, and that their representation by the broken curves of the compound theory be markedly superior to any other mode of representation.

It is safe to say that as the number and precision of the measurements are increased, their representation by broken curves, as opposed to continuous

[29] F. Zwicky, *Proc. Nat. Acad. Sci.*, **17**, 524 (1931).
[30] See footnote 26.
[31] R. Wietzel, *Z. anorg. allgem. Chem.*, **116**, 71 (1921).
[32] G. E. Gibson and W. F. Giaque, *Jour. Amer. Chem. Soc.*, **45**, 93 (1923).
[33] L. H. Adams, *Jour. Franklin Inst.*, **216**, 39 (1933).

curves, becomes increasingly improbable. For example, consider the specific volume of the Na_2O–SiO_2 and Na_2O–CaO–SiO_2 glasses. The earlier measurements were made on glasses which were not analyzed, of uncertain composition, not heat-treated or annealed, and often measured on fire-polished surfaces, and deductions drawn from them may be dismissed from consideration. Later Turner,[34] making use of the density measurements of Peddle,[35] expressed the specific volume by two straight lines intersecting at the composition of $Na_2O{\cdot}2SiO_2$. The measurements were made on glasses which were

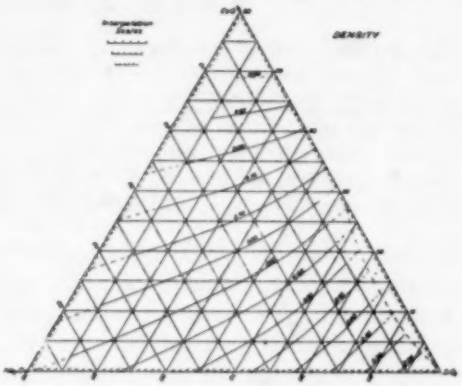

FIG. 8.—Relation between density and composition in the ternary system, Na_2O–CaO–SiO_2.

not analyzed, but the compositions were calculated from the proportions of the ingredients melted. Winks and Turner[36] later made more accurate measurements on a more extensive series of analyzed glasses, and found that the results were better expressed by a continuous curve. Glaze, Young, and Finn[37] made accurate measurements on glasses of known composition in the binary system, Na_2O–SiO_2, and also in the ternary system, Na_2O–CaO–SiO_2, and concluded that in the binary glasses the results were better expressed by four straight lines, implying the assumption of three silicate compounds, $2Na_2O{\cdot}3SiO_2$, $Na_2O{\cdot}2SiO_2$, and $Na_2O{\cdot}3SiO_2$, of which $2Na_2O{\cdot}3SiO_2$ and $Na_2O{\cdot}3SiO_2$ are entirely hypothetical. It is evident from an inspection of their curves that this interpretation is not a necessary one, and replotting their results confirms this conclusion.[38] When they go into the ternary system they abandon the hypothesis of compound formation.

The most extensive group of results on this system is that of Morey and Merwin,[39] who have measured glasses well distributed over the entire ternary system from mixtures intermediate between the orthosilicate and the metasilicate ratios to SiO_2. Their results for density and refractive index are shown in Figs. 8 and 9. They say,

> These final interpolations, especially along the refrac-

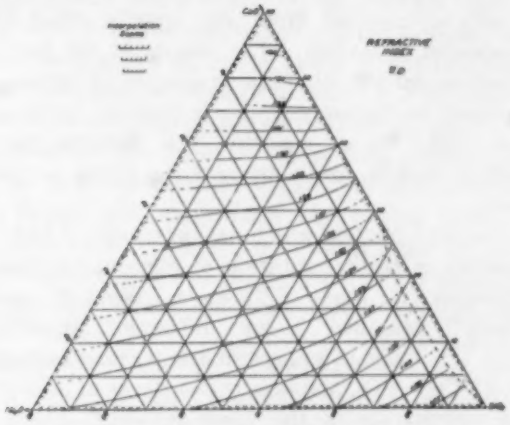

FIG. 9.—Relation between refractive index and composition in the ternary system, Na_2O–CaO–SiO_2.

> tive-index curves, 1.52 to 1.55, and the density curves, 2.50 to 2.65, include so many data that they might be expected to indicate whether or not the isocurves should be continuously curved or segmented into two or three less curved lines. No evidence of such segmentation was found. However, each might be replaced by three "best" straight lines without producing departures greater than the departures of single observations, but the distribution of departures would be too systematic to be tolerated.

Morey and Merwin calculated the specific refractivity of all of their glasses by four different formulas which have been proposed, namely, the Gladstone-Dale, Lorentz-Lorenz, Eykman, and Lichtneker formulas. For each equation the specific refractivity was calculated by assigning to each oxide an arbitrary constant value and assuming that the specific refractivity is a linear function of the composition. Except for the Lorentz-Lorenz formula, the constant used for SiO_2 glass was that calculated from the best

[34] W. E. S. Turner, *Jour. Soc. Glass Tech.*, **9**, 147 (1925).
[35] C. J. Peddle, *ibid.*, **4**, 1 (1920).
[36] F. Winks and W. E. S. Turner, *ibid.*, **15**, 185 (1931).
[37] F. W. Glaze, J. C. Young, and A. N. Finn, *Bur. Stand. Jour. Research*, **9**, 799 (1932).
[38] E. Preston and W. E. S. Turner (see footnote 9) reach the same conclusion.
[39] See footnote 26.

values of refractive index and density, as given by Sosman.[40] The other two constants were adjusted to give a fairly uniform distribution of positive and negative departures. The results are expressed in triangular diagrams showing the departures as a function of composition. The surface of specific refractivity is evidently one with a double curvature, and the figures represent the distance of this curved surface above or below an arbitrary inclined plane obtained on the additivity hypothesis. The specific refractivity is evidently roughly additive, and the departures from the additive relationship are not such as would be expected from any specific effect of compound formation. The results of the many observers on the physical properties of glass at ordinary temperatures indicate that no justification exists for an assertion that definite compounds exist in, and determine the properties of, glass.

A second method which has been applied to the problem of the constitution of glass at low temperatures is that of X-rays. Wyckoff and Morey[41] obtained X-ray diffraction patterns from a number of glasses in the ternary system, Na_2O–CaO–SiO_2, and also the patterns of crystalline compounds in the same system,[42] and established the fact that the type of pattern obtained depended on the composition of the glass. In some cases the broad band patterns typical of liquids were obtained, while with other compositions the narrower bands were as sharp as those obtained from crystals of colloidal dimensions. In glasses high in SiO_2 these bands only roughly corresponded to the strong band from cristobalite crystals. Attempts to prove correspondence between the glass pattern and that of the crystalline compound, which should separate, failed. For example, $Na_2O{\cdot}2CaO{\cdot}3SiO_2$ is a definite compound whose structure has been approximately determined, and a glass of this composition gives a diffuse line pattern. When the glass was slowly crystallized, instead of the diffuse lines sharpening into the lines characteristic of the crystal, it was evident that the two patterns were not the same.[43] That the glass was crystallizing could be seen with the eye before it could be detected on the X-ray plate. Later,

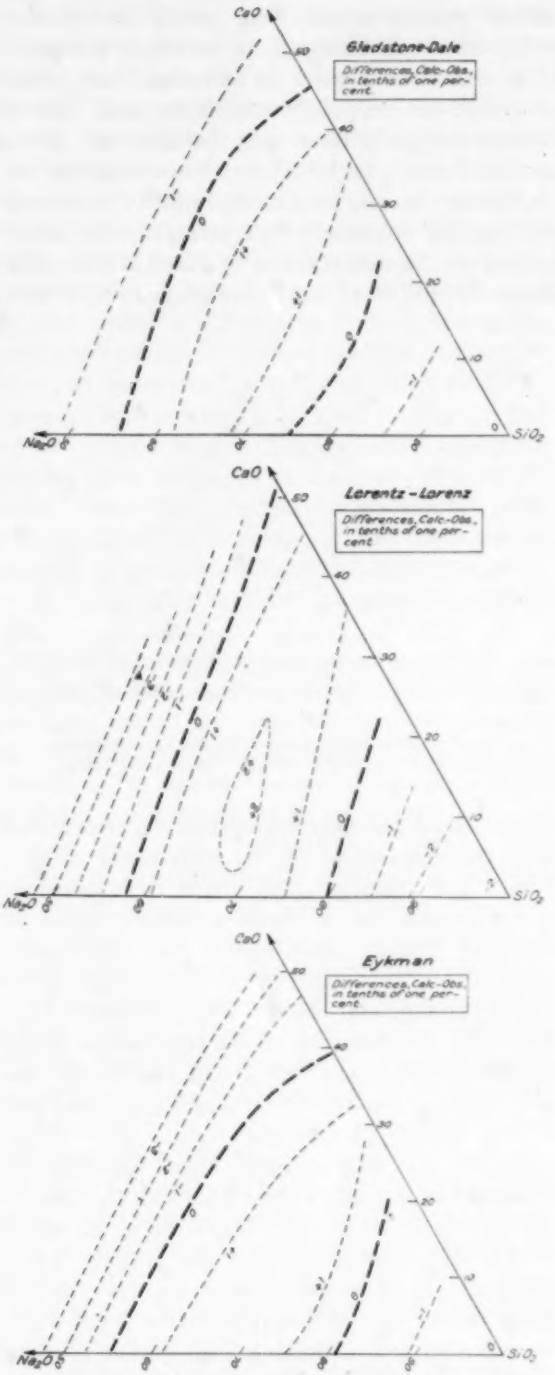

FIG. 10.—The percentage deviations from an additive relationship between composition and specific refractivity calculated by means of (*a*) the Gladstone-Dale formula $(n-1)/d$; (*b*) the Lorentz-Lorenz formula $[(n^2-1)/(n^2+2)]\cdot 1/d$ and, (*c*) the Eykman formula $[(n^2-1)/(n+0.4)]\cdot 1/d$.

[40] R. B. Sosman, The Properties of Silica. Chemical Catalog Co., New York, 1927.

[41] R. W. G. Wyckoff and G. W. Morey, *Jour. Soc. Glass Tech.*, **9**, 265 (1925).

[42] *Ibid.*, *Amer. Jour. Sci.*, **12**, 419 (1926).

[43] Unpublished results of R. W. G. Wyckoff and G. W. Morey.

Parmelee, Clark, and Badger[44] concluded that the diffuse-ring type of pattern indicates incipient crystal formation. Clark and Amberg[45] concluded that the SiO_2 molecule is the unit of structure in SiO_2 glass, the molecules being arranged end to end in long chains, the chains grouped into bundles. Some details of their experimental work have not been confirmed. Randall, Rooksby, and Cooper[46] obtained essentially the same results as previous workers, but drew therefrom far-reaching conclusions. From the limited resemblance of the patterns of amorphous precipitated silica and of silica glass to that of high cristobalite they say:

> It follows, then, that there is little structural difference between these two forms of silica. In this sense the workers who hold to the "amorphous" theory of glasses are correct. The essential point is that the term "amorphous" has no meaning. The difference between the crystalline state, on the one hand, and the "vitreous" and "amorphous" on the other, is one of degree, not of kind.

In the discussion,[46b] Randall states, "In ordinary vitreous silica he thought it quite reasonable to say there must be some 80% of cristobalite." Probably none of the more recent workers would venture such categorical statements.

Zachariasen[47] has published an interesting paper on the structure of glass. He says,

> ...the atoms in glass must form an extended three-dimensional network. From the results of X-ray diffraction experiments it follows, however, that this network is not periodic and symmetrical as in crystals. Yet it is not entirely random due to the fact that the internuclear distances do not sink below a given minimum value. All atomic distances are for this reason not entirely probable and X-ray patterns of the type observed will be a direct consequence. If we make use of crystal structure terminology, we may say that the network in glass is characterized by an infinitely large unit cell containing an infinite number of atoms. Because of the lack of periodicity no two of the atoms are structurally equivalent....

This picture of the structure of glass seems much more probable than that of Randall, Rooksby, and Cooper, but after all does it do much more than to say, in the language of X-ray structure, that glass is an undercooled liquid? To be sure there is a greater definiteness in the statement that the atoms are in a network, but the picture of the structure of liquid water given by Bernal and Fowler[1] is almost as definite as this. There is an increasing amount of evidence that liquids do possess a structure. In nonpolar liquids the tendency is for a structure the unit of which is molecular, such as the parallel orientation of the paraffin hydrocarbons. In polar liquids the structure is atomic; but in all cases definitely lacking in periodicity.

Zachariasen's further discussion is based on the assumption, also made by others, that the energy difference between crystal and glass is small, but that assumption is, as far as the writer is aware, without experimental foundation. The latent heats of melting of few crystalline silicates are known. While the accuracy of these is questionable, they indicate that silicates are characterized by latent heats of melting higher than those of most other compounds, and some of those silicates most prone to form glasses have larger heats of fusion than others which are readily crystallized. The latent heats of silicates determined by Mulert[48] average about 70 calories per gram. The latent heat of crystallization of orthoclase is 83 calories per gram, that of leucite 26, the lowest of any silicate measured. But orthoclase can not be crystallized, and leucite can not be quenched to a glass. Goranson and Kracek[49] found 35 calories per gram for $K_2O{\cdot}4SiO_2$. The melting point of this compound is 765°, and it probably is the most difficult to crystallize of any binary silicate. Comparison with the latent heats of melting of substances which can not be obtained as glass[50] will show that silicates, instead of having a low energy difference between the crystalline and liquid forms, have in fact a high energy difference. The latent heat of fusion of KNO_3, for example, is only about 25 calories per gram. This large part of Zachariasen's theoretical treatment, while it correctly indicates that certain oxides, including silica and boric oxide, can be obtained as glass, is founded on an erroneous assumption.

Warren[51] has recently presented a more definite picture of the structure of silica glass, a structure based primarily on experimental results. In harmony with previous workers, he found that the

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[44] C. W. Parmelee, G. L. Clark, and A. E. Badger, *Jour. Soc. Glass Tech.*, **13**, 285 (1929).
[45] G. L. Clark and C. R. Amberg, *ibid.*, p. 290.
[46] (*a*) J. T. Randall, H. P. Rooksby, and B. S. Cooper, *Jour. Soc. Glass Tech.*, **14**, 219 (1930).
(*b*) *Ibid.*, **15**, 54 (1931).
[47] W. H. Zachariasen, *Jour. Amer. Chem. Soc.*, **54**, 3841 (1932).
[48] O. Mulert, *Z. anorg. allgem. Chem.*, **75**, 238 (1912).
[49] R. W. Goranson and F. C. Kracek, *Jour. Phys. Chem.*, **36**, 913 (1932).
[50] International Critical Tables, V, p. 131.
[51] B. E. Warren, *Z. Krist.*, **86**, 349 (1933).

X-ray patterns of both vitreous silica and of Pyrex brand chemical-resistance glass show a single broad diffraction ring whose maximum corresponds to a value of 4.32 Å for the spacing in silica. Warren discusses the two possible explanations of the observed diffraction pattern and rejects that explanation which ascribes the pattern to crystallites of cristobalite, the rejection being on the basis of discrepancies in the calculated spacing, in the volume-temperature relations, and the behavior of the material on heat treatment. The accepted hypothesis is based on scattering from a noncrystalline random network, in which each silicon is tetrahedrally surrounded by four oxygens and each oxygen is shared by two tetrahedral groups. The nearest neighbors of any tetrahedral group are approximately fixed in position, but beyond this the spacing is wholly random. The X-ray spacing from such a random network was calculated using Zernicke and Prins' method of treating the problem of diffraction in liquids, with satisfactory agreement between the observed and calculated results.

The picture of the structure of glass worked out by Warren is in agreement with that assumed by Zachariasen, in that the arrangement of the atoms is essentially random, and the network is nonrepeating and nonsymmetrical. The structure given by Warren is more definite, since it is based on experimental evidence, and in it the tetrahedral group of oxygen atoms surrounding the silicons, which plays so important a part in all crystalline silicate structures, is the leading feature. As applied to the constitution of glass these structures lend no support to those who attempt to explain the properties of glass by the presence of definite compounds. The glassy structures are in conflict with any such assumption, but they are completely in harmony with that picture of the constitution of glass which has been emphasized in the preceding discussion.

V. Summary

A discussion of the constitution of glass necessarily involves a discussion of the details of the atomic and molecular arrangement of the materials of which the glass is composed. That such information can be obtained with gaseous mixtures has long been known and more recent work has enabled us to form plausible hypotheses as to the atomic arrangement in crystalline substances. But in liquids, whether they be pure liquids or solutions, and whether the solutions be aqueous ones at ordinary temperatures or silicate mixtures at high temperatures, we have no method of obtaining definite information as to the atomic and molecular condition of the constituents. The various types of evidence which have been used as the basis of hypotheses concerning the constitution of glasses are discussed in three categories, namely, the properties of glass at high temperatures, in the annealing range, and at ordinary temperatures. The available evidence in each of these categories has been critically discussed and it is concluded that there is no support for the hypothesis that definite compounds are formed in the glass at any temperature.

At high temperature, glasses are complex solutions concerning which we may make the assumption that they contain statistical representatives of the many possible molecular species capable of being formed by the components. The proportions of these species will be determined by the potential requirements of the various atoms at the temperature in question, and will change with temperature in accordance with the usual laws governing equilibrium in homogeneous systems.

As the temperature is lowered and the viscosity increases, the rate at which the homogeneous equilibrium is attained will decrease until, at ordinary temperatures, the rate of change of the internal structure will be practically zero. The atoms will then be fixed in the positions corresponding to the temperature at which they were frozen in, and the temperature region in which they become frozen in will be a critical one with respect to the properties of the glass. By critical is meant that while at higher temperatures, at which the attainment of equilibrium is practically instantaneous, and at lower temperatures, where the rate is very small, alteration of the duration of heat treatment is without measurable influence on the final properties, while within the critical region the extent to which the equilibrium configuration is attained, and hence the values of the properties, will depend on the duration of the heat treatment.

Glass at the ordinary temperatures represents a liquid the viscosity of which has reached so high a value that for all practical purposes it is rigid. Recent studies by means of X-rays lend support to this conception of the constitution of glass.

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VISCOSITY AND ELECTRICAL CONDUCTIVITY OF MOLTEN GLASSES*

By C. L. Babcock

ABSTRACT

Using a new type of concentric cylinder viscosimeter, the viscosity, η, and electrical resistivity, ρ, of some commercial glasses and the glasses of the soda-silicate system have been investigated in the region of 700 to 1400°C corresponding from 3 to 10^7 poises and from 0.3 to 10^8 ohms. The results in the viscous region show proportionality between log η and log ρ in the region investigated. In the two glasses investigated at lower temperatures, it can be seen that the same constants do not hold throughout the whole region. These results are discussed considering the kinetic picture of liquids (see summary).

I. Introduction

The determination of the viscosity of molten glass is of fundamental importance for the understanding of the manufacturing process. The connection between viscosity and other properties might lead not only to a control of the manufacturing process, but also to a better understanding of the constitution of glass.

Washburn and Shelton[1] give a rather complete account of the work done in the measurement of the viscosity of glass prior to 1925.

These authors and English[2] used the Margule's method for measurements above 750°C. In this method the glass occupies the annular space between two concentric cylinders, one of which is fixed while the other is rotated at a constant speed.

Lillie[3] used a variation of the Margule's method for measurements in the viscosity range 10^1 to 10^8 poises. In the range 10^1 to 10^4 the outside cylinder was rotated at a constant determined speed and the torque on the inner cylinder was measured by means of a steel torsion wire.

Stott, Irvine, and Turner[4] made measurements in the range 10^2 to 10^4 poises by determining the rate of fall through molten glass of a partially counterpoised platinum-iridium ball suspended on a wire of the same material. The system was calibrated by means of syrup.[5]

J. T. Littleton[6] has given a rather complete survey of the recent work in "The Thermal Treatment of Glass."

II. Description of Apparatus

Karl Lark-Horovitz suggested to the author the design of an apparatus, using the concentric cylinder method which would measure the viscosity and electrical conductivity of molten glass simultaneously. He suggested that the inner cylinder be mounted rigidly upon a rod and that this rod operate a special type of precision balance, the null method of balancing to be used. In this method the electrical connections would be made to the platinum inner and outer cylinders.

Together with Hoffacker,[7] the writer has designed and constructed this apparatus according to the above suggestions, and this method has been used for measuring the viscosity and electrical conductivity of commercial glucose solutions.[8] In this case the viscometer was calibrated with castor oil. The following apparatus for measurements on the viscosity and electrical conductivity of molten glass was used.

Figures 1, 2, 3, 4, and 5 show the details of the apparatus. Figure 1 shows the assembled apparatus during a test run.

The glass case which covers the torque meter (*TM*) was removed while the photograph was being taken. The instrument is mounted upon a plate of $\frac{1}{2}$-inch steel 20 inches wide and 26 inches long. This base rests upon three leveling screws. Three brass tubes (1-*LT*) $1\frac{3}{4}$ inches outside diameter and 30 inches long are mounted upon this base. They are placed at the vertices of an equilateral triangle whose sides are $13\frac{1}{2}$ inches long.

The torque meter (1-*TM*) is mounted upon a $\frac{1}{2}$-inch aluminum plate (1-*AP*) cut in the shape of a hexagon.

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* Presented at the Annual Meeting, American Ceramic Society, Cincinnati, Ohio, February, 1934 (Glass Division). Received April 26, 1934.

Contribution from the Purdue Physical Laboratories.

This work was started in 1929, carried out under a Research Fellowship of the Corning Glass Works 1930–32, and has been continued since then.

[1] E. W. Washburn and G. R. Shelton, *Univ. of Ill. Eng. Expt. Sta. Bull.*, No. 140, April, 1924.

[2] S. English, *Jour. Soc. Glass Tech.*, **7**, 25 (1923); **12**, 106 (1928).

[3] H. R. Lillie, *Jour. Amer. Ceram. Soc.*, **12** [8], 505–29 (1929).

[4] V. H. Stott, E. Irvine, and D. Turner, *Proc. Roy. Soc.*, **108**, 154 (1925).

[5] Recently Hunter has developed a method of measuring viscosity by the falling-sphere method, using radio control circuits and has realized a high degree of accuracy (see R. G. Hunter, *Jour. Amer. Ceram. Soc.*, **17** [5], 121–27 (1934).

[6] J. T. Littleton, *Jour. Soc. Glass Tech.* [*Trans.*], **15**, 262 (1931).

[7] C. L. Babcock and J. V. Hoffacker, *Phys. Rev.*, **44**, 321*a* (1933).

[8] C. L. Babcock, M.S. Thesis, Purdue Univ., 1931.

This aluminum plate was mounted upon three brass tubes (1-*ST*) 1½ inches in diameter and 20 inches long. These tubes were accurately machined and telescoped into the three tubes mounted on the steel base. Three brass clamps (1-*C*) with knurled headed screws were machined to fit around the inside tubes. It is thus possible to move the torque meter and frame up and down at will and to secure it in any desired position by means of the three clamps.

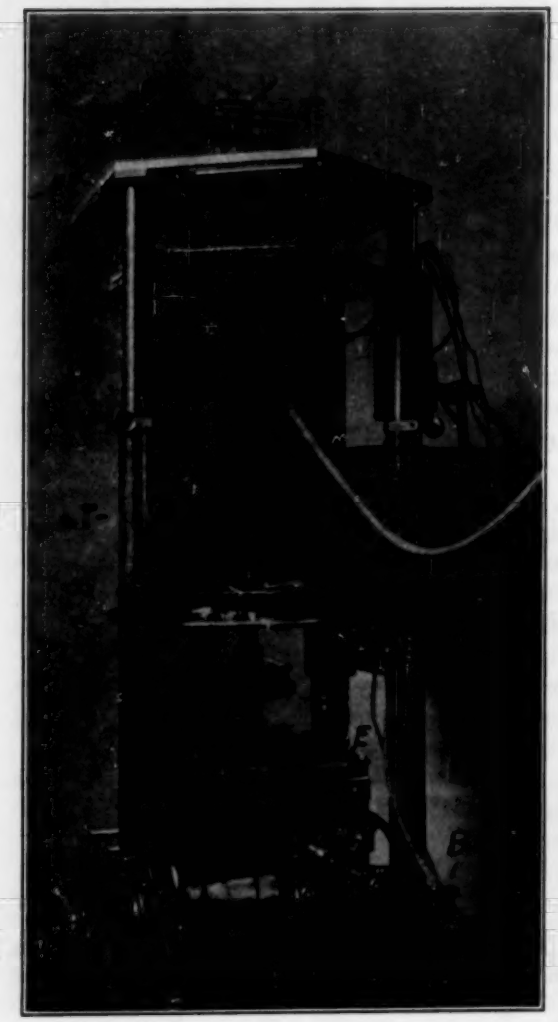

FIG. 1.—Complete apparatus.

The outer platinum cylinder (*B*, Fig. 2), 1 inch diameter and 1½ inches high, fits into a sillimanite tube. The sillimanite tube and outer cylinder may be centered and removed from the centering device at any time without disturbing the adjustment. A platinum wire is fused on to the rim of the platinum outer cylinder and this wire is led down through a hole (*H*, Fig. 2) in the sillimanite tube. This wire is brought down alongside the platinum cylinder and fits into notches made through the two rings which project from the inside of the sillimanite tube and hold the outer platinum cylinder in place. This arrangement prevents the outer cylinder from turning in the holder.

The platinum wire is brought out of the sillimanite holder and electrical connection is made for electrical conductivity measurements. The outer cylinder assembly can

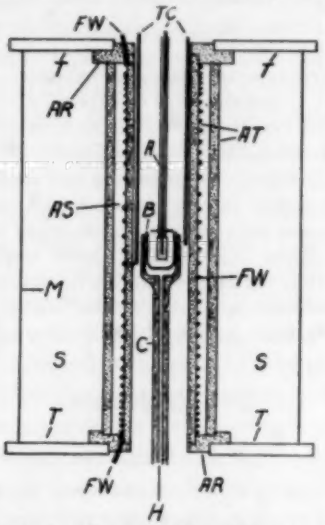

FIG. 2.—Cross-section of furnace.

be moved, within certain limits, in a horizontal plane, and its axis can also be adjusted so that it will make small angles with a true vertical axis. The adjustment for in-

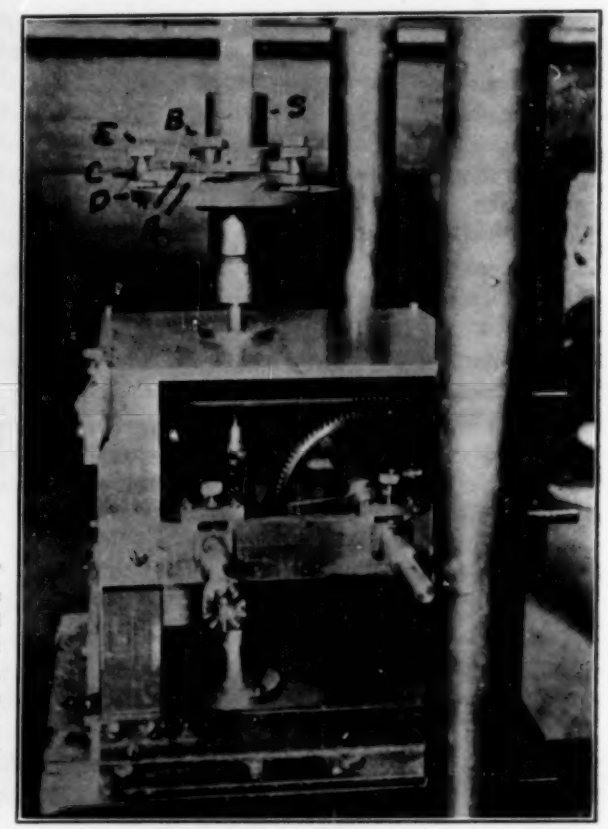

FIG. 3.—Gear train and centering device.

clining the axis of rotation was necessary because the sillimanite tubes had been bent slightly when they were fired.

The outer cylinder assembly and centering device rest upon the top of a $^1/_2$-inch diameter vertical steel shaft. This steel shaft passes through bearings in the bottom and top of the frame of a worm gear box (Fig. 3) and rests upon the end of a micrometer screw which is mounted in the bottom of the gear box. A ball-thrust bearing separates the lower end of the vertical shaft and the top of the micrometer shaft. A special arrangement allows the whole outer cylinder assembly to be moved up and down by means of the micrometer screw. The distance between the inner and outer cylinders can be accurately determined.

An 1800-r.p.m. 60-cycle synchronous motor is used to rotate the outer cylinder. A built-in reduction unit reduces the speed in the ratio of 54 to 1. The motor is connected to a spur gear train (1-*B*) which further reduces the speed. The worm gear train is mounted directly under the viscosity apparatus. It consists essentially of three sets

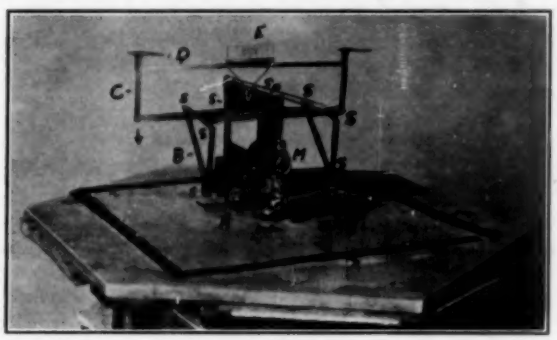

FIG. 4.—Torque meter.

of worms and worm gears each of which reduces the speed. The spur gear train reduces the speed 625 to 1 in steps of 5 to 1 and the worm gear train $96^3 (= 884736)$ to 1 in steps of 96 to 1. The speed of the shaft leading to the spur gear train is 3.48 radians per second. Thus speeds may be obtained from 3.48 radians per second down to 3.48 times $10^{-8.74}$ radians per second. The lowest speed used in the work to be reported at this time was $3.48 \times 10^{-4.78}$ radians per second.

Figures 4 and 5 show the details of the torque meter. The device used to measure the torque is entirely new and unique. Its working has to be clearly understood to interpret the results obtained with the instrument.

The torque meter is mounted so that the platinum inner cylinder is concentric with the platinum outer cylinder. The inner cylinder (2-*A*) assembly consists of a hollow platinum rod 13 inches long and $^3/_{16}$ inch in diameter. The inner cylinder proper is formed upon the lower end of this rod and is 1 inch long and $^1/_4$ inch in diameter. A guard ring made of platinum is mounted $^1/_4$ inch above the top of the inner cylinder proper to prevent the glass from being contaminated. The arrows show the direction of rotation of the rod. The brass bar (4-*A*) is attached to the inner cylinder rod and turns with it. This brass bar is rigidly mounted upon a vertical brass bar carrying the mirror (4-*M*) and is connected to the frame of the torque meter by means of two phosphor bronze suspensions (4-*S*) which are 0.006 inch thick and $^1/_{16}$ inch wide. The separation between the vertical bar and the frame is $^1/_8$ inch. The vertices, two triangular-shaped brass frames (4-*B*) are connected by phosphor bronze wires (4-*S*) to the bar (4-*A*), to the scale frame (4-*C*), and to a bar which is mounted rigidly on the frame. The scale (4-*D*) and the scale frame (4-*C*) are suspended from the center of the frame by two phosphor bronze suspensions (4-*S*). When the inner cylinder is subjected to a torque the various moving parts are displaced for limited distances in the directions indicated by the arrows. In this way a rotation of the inner cylinder about a vertical axis is transformed into a rotation by the scale (4-*D*) about a horizontal axis. The torque exerted on the inner cylinder is counterbalanced by placing weights

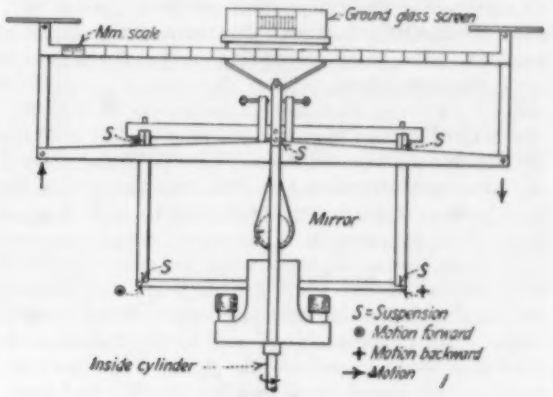

FIG. 5.

on the scale in the usual way. A spring (4-*Sp*) regulates the vibration of the meter about its zero position and serves to make the adjustment more critical. The whole torque meter is covered with a glass case because of its sensitivity to air currents.

Figure 5 shows the other side of the torque meter as it appears to the person who is using it to make measurements.

The torque meter is balanced with the aid of an optical lever arrangement. An 18-foot optical lever makes it possible to make quite accurate adjustments.

Figure 2 shows the details of the furnace.

The power is taken from the low side of a transformer which steps the voltage down from 220 to 55. The current through the furnace coil is controlled by means of a large carbon rheostat in the primary circuit. The coil is wound with wire, having the composition 80% platinum and 20% rhodium. The inside tube (2-*AT*) is made of Alundum and is 14 inches long and 2 inches inside diameter. A larger Alundum tube (2-*AT*) is placed concentric with the inner tube and the two are separated by the air space (2-

AS). Alundum rings (2-*AR*) are placed at both ends of the tubes as shown in the drawing and are sealed to the tubes with Alundum cement. The ends of the furnace coil are led out at both ends of the furnace as indicated (2-*FW*). The whole assembly is enclosed in a metal tube (2-*M*), 10 inches in diameter, and the space between this metal tube and the outer Alundum tube is packed with Sil-O-Cel powder. The plates at the ends of the furnace are made of $\frac{1}{2}$-inch transite board (2-*T*). The turns of the furnace coil are closer together at the top and bottom than they are in the middle. This was done in order to obtain as large a space as possible in the center of the furnace which would have the same temperature throughout. The temperature is the same for a distance of about 3 inches along the tube in the center of the furnace. Since the outer platinum cylinder is 1 inch in diameter and $1\frac{1}{2}$ inches high, it can be seen that the glass mass is kept in a region of the furnace which has the same temperature throughout.

Temperatures are measured by means of three thermocouples having the composition platinum against 90% platinum and 10% rhodium. One thermocouple is placed inside the hollow platinum rod (2-*A*) so that the junction is inside the inner cylinder proper. It is secured in a position about $\frac{1}{4}$ inch from the bottom of the inner cylinder proper. The ends of the two thermocouple wires leading from the hot junction dip into two mercury cups (4-*T*) and wires of the same compositions lead from the mercury cups to the cold junction which is kept in melting ice in a thermos flask. This arrangement is necessary because temperature measurements are taken while the inner cylinder is subjected to a torque. This method is quite satisfactory as shown by calibration data against a standard thermocouple. The temperature indicated by this thermocouple is taken as the temperature of the glass. Two other thermocouples are placed out in the space between the furnace wall and the outer cylinder holder in order to determine whether or not the furnace has reached a constant temperature. One thermocouple is placed on a level with the top of the glass mass and the other is placed on a level with the bottom of the glass mass. These two thermocouples are held in place by means of a lava ring which extends down within the inside furnace tube for a distance of 2 inches. The inside diameter of the lava ring is $1\frac{1}{2}$ inches. These thermocouples are led out through the packing at the top of the furnace to the cold junctions in the thermos flask. A Brown potentiometer accurate to 2 microvolts was used to measure the electromotive force of the thermocouples.

The electrical resistance of the glass was measured by means of the usual Kohlrausch bridge method. The electrical connection to the platinum inner cylinder was made through the mercury cup (4-*T*) and that to the outer cylinder through the sillimanite holder as described above. Connection to the outer cylinder was not made while the outer cylinder was turning. Alternating current of 500 cycles and 10 volts having a true sine curve form was used. Head phones were used in order to determine the balance position of the bridge arrangement.

III. Preparation of Glasses (Na_2O-SiO_2)

Two glasses (47% SiO_2–53% Na_2O) and (81% SiO_2–19% Na_2O) were melted at the Corning Glass Works.

The materials used were of the standard variety used at Corning and the approximate analyses were as follows:

Sand, 99.70%, 0.02Fe_2O_3, 0.02TiO_2, remainder chiefly Al_2O_3.

Soda, 99.80%, Na_2CO_3, with traces of sodium sulfate and sodium chloride.

Niter, 99.50%, $NaNO_3$ with 0.2 to 0.3 moisture and traces of sodium chloride and sodium sulfate.

These glasses were melted in 100-pound pots of standard clay in one of the regular furnaces in which the glass reaches a temperature of approximately 1350°C. The process of melting was to fill in batch, close the pot, and allow to melt for 5 to 6 hours; dip out into water, fill the pot again with batch, and at the end of 4 to 5 hours add the cullet which was obtained from the first dipping into water. After the final filling, the glass was allowed to melt from 10 to 12 hours after which all of the material was ladled out into the water, then dried and broken up.

The glasses were, after the melting at Corning, not clear and homogeneous. They were then melted in the Purdue Laboratory in an 80% Pt 20% Rh crucible having a capacity of 75 cc. The 47SiO_2 glass was heated in this crucible for about 3 hours at 1250°C and stirred frequently with a Pt-Rh stirring rod. The 81% SiO_2 glass was heated for 5 hours at 1350°C and was frequently stirred with the Pt-Rh rod.

These two glasses were then poured into clean graphite molds and allowed to cool after which the chemical compositions were determined.

Definite portions of the two glasses were then used to form glasses having 60, 65, and 73% SiO_2.

The melting procedure was the same for all five glasses.

All other glasses, with the exception of 1 BS(16^{III}), were also furnished by the Corning Glass Works.

TABLE I
Glasses Investigated

No.	SiO_2	RO	K_2O	Na_2O	Al_2O_3	
1	47.3			52.1	0.3	
2	60.0			39.2	0.7	
3	65.4			34.0	0.3	R_2O_3
4	72.9			26.5	0.7	
5	81.0			18.4	0.3	
6	72.6	6.40 (CaO) 1.7 (MgO)	0.68	16.0		1.00 R_2O_3 1.43 B_2O_3
7	70.12	8.77 (CaO)	tr	21.1	0.02	
1BS	67.3	7.00 (CaO) 7.00 (ZnO)		14.0	2.50	2.00 B_2O_3 0.2 Mn_2O_3
2BS	81			4	2	13 B_2O_3
3BS	75			10	5	10 B_2O_3
4BS	75	5 (PbO)		5		15 B_2O_3
5BS	56	20 (BaO)	10	4	$2\frac{1}{2}$	$7\frac{1}{2}$ B_2O_3
1LB	65	20 (PbO)	$7\frac{1}{2}$	$7\frac{1}{2}$		
2LB	60	30 (PbO)	5	5		

IV. Method of Making Measurements

The measurements are made in the following way:

The outer platinum cylinder is put into the sillimanite holder with the platinum wire, which is welded to the rim, brought down through the hole in the tube and led out at the bottom by means of porcelain tubing. This wire provides electrical connection to the outer cylinder. The holder is placed in the centering device which is then adjusted until the outer cylinder rotates about a vertical axis. The platform which holds the torque meter and inner cylinder assembly is lowered into place. The torque meter and inner cylinder assembly are adjusted so that the inner and outer cylinders are concentric. The outer cylinder assembly is raised by means of the micrometer screw until the bottom of the outer cylinder touches the bottom of the inner cylinder. The outer cylinder is then lowered a distance of 9.52 mm.

After these adjustments are made, the torque meter and inner cylinder assembly are removed and the electric furnace is put into place with the outer cylinder in the center of the furnace where the whole space surrounding it is at the same temperature. The bottom of the furnace is packed with rock wool, held in place by pieces of transite board bolted to the lower end of the furnace. The rock wool is pressed in toward the sillimanite holder from all directions and the transite board bolted to keep the rock wool tightly packed around the tube.

The outer cylinder is then filled with glass and the hole in the top of the furnace, $1^1/_2$ inches in diameter, is covered with pieces of mica and transite board. The current in the furnace is turned on and regulated so the glass mass will heat slowly. Glass is added from time to time until the volume of the glass mass is 12 cc.

The inner cylinder is lowered into place when the temperature of the glass is about 1200°C. Forms of Alundum, cut so that they fit around the inner cylinder rod, are then put over the small opening at the top of the furnace. The clearance between the inner cylinder rod and these forms is $^1/_{16}$ inch. It has been found necessary to direct a blast of air across the top of the furnace normal to the rod and the convection currents coming out of the furnace. This prevents the convection currents from disturbing the balance and also serves to keep the measuring apparatus cool.

The optical lever arrangement for balancing the torque meter is adjusted so that the light beam is focused on an arbitrary line of the ground glass scale.

After the temperature of the glass and the space out in the furnace has been constant for at least 30 minutes the rotating apparatus is turned on. The two thermocouples out in the space between the rotating outer cylinder and the walls of the furnace register the same temperature readings when the furnace has reached a constant temperature. The torque, which is exerted on the inner cylinder, causes the light beam to move over the ground glass scale. The light beam moves over to a definite position and is quite steady. Enough weights are placed on the brass scale to bring the light beam back to the original "zero" position. The torque as registered by the brass scale is expressed in gram-centimeters. Weights of 10, 200, 300, and 500 milligrams have been used for this purpose. At the high temperatures, readings can be taken quite easily in 5 minutes, but at the lower temperatures near the softening point, from 1 to $1^1/_2$ hours are required.

The inner and outer cylinders were then connected electrically to one arm of the 500-cycle a.c. bridge and the electrical resistance of the glass was determined. Both cylinders were stationary while the electrical measurements were being taken.

V. Calibration of Instrument

The instrument was calibrated with two soda-lime-silica glasses previously measured by H. R. Lillie of the Corning Glass Works.

The torque, indicated on the torque meter in gram-centimeters, was multiplied by the ratio of the highest speed, 3.5 rad./sec., to the speed used. At 900°C, for example, the speed reduction was 625 and the torque was 2.25 gram-centimeters. The product, 1406, times a constant equals the viscosity at this temperature. Lillie's value of viscosity at this temperature is 64,269 poises. The constant in this case is 45.7. The temperature interval from 900 to 1217°C was chosen for calibration purposes since temperatures below and above this interval are attended by greater possible errors. This calibration factor, of course, depends on the constants of the apparatus, especially the phosphor-bronze suspensions. Calibration at different times after changing suspensions has been carried out and the values were 44.3, 87, 63, and 101.

TABLE II

Glass No. 6

Speed reduction	Torque (gm.-cm.)	Log viscosity	Log resistivity	°C	$1/T \times 10^4$
625	3.25	4.953	1.263	880	0.867
25 × 96	0.44	4.657	1.171	904	.849
125	1.40	3.883	0.896	1013	.777
625	2.25	4.794	1.242	900	.852
625	2.20	4.784	1.200	902	.851
25	2.16	3.378	0.769	1101	.728
25	0.78	2.936	0.587	1196	.681
625	1.65	4.659	1.152	918	.839
125 × 96	1.66	5.946	1.557	794	.937
125 × 96	1.68	5.950	1.580	790	.941
125 × 96	5.90	6.496	1.764	748	.979
125 × 96	7.28	6.587	1.764	746	.980
125 × 96	7.40	6.594	1.764	747	.980
25	0.58	2.807	0.544	1217	.671
25	0.20	2.345	0.340	1337	.621
625 × 96	2.00	6.725	1.850	731	.996
625 × 96	1.60	6.628	1.825	736	.991
625 × 96	2.00	6.725	1.843	734	.993
625 × 96	1.60	6.628	1.816	738	.989

The platinum conductivity cell was calibrated in the usual way with 0.1 and 0.01 normal KCl solutions. Resistances were multiplied by 9.92 in order to convert them to specific resistances. The resistance of the leads to the cell containing the glass was determined as a function of tempera-

ture throughout the region investigated. Corrections to the ratio readings of the bridge and for lead resistance were made in all cases. A typical set of readings is reproduced below. Measurements were taken in the order given.

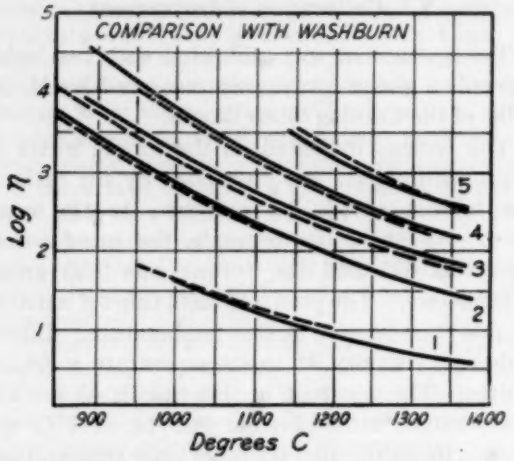

FIG. 6.—Soda-silica glasses; comparison with Washburn and Shelton. Log η against °C.

Considerable difficulty was encountered in making measurements on the soda-silica glasses, especially glasses 1 and 5, due to the relative ease with which they devitrified. In some cases results were obtained below the liquidus temperatures which lie on the curve for the viscous region, but in most cases the values of viscosity in

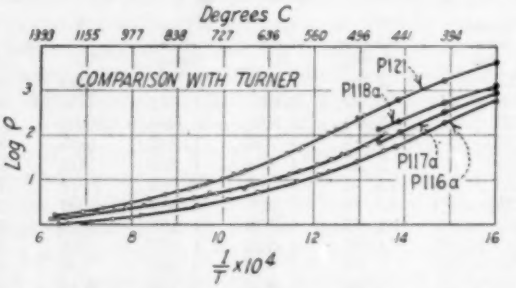

FIG. 7.—Soda-silica glasses are indicated by circles; comparison with Turner, by circles with center dot. Log ρ against $1/T \times 10^4$.

this region were abnormally high, indicating devitrification.

Washburn and Shelton found that the ratio of viscosity to torque varied from 0.56 to 2.7 when the value of log η changed from 0.25 to 5. There seems to be no fundamental reason for this, and other investigators[9] have found that Washburn and Shelton's results have to be corrected to bring them into reasonable agreement with their own. The broken lines in Fig. 6 show Washburn and Shelton's corrected values for glasses which have approximately the same composition as those reported here (shown by the solid lines).

Specific resistances of glasses 2, 3, and 4 were taken at such low temperatures as to overlap the region in which Turner[10] made measurements. Glasses 1 and 5 devitrified, and measurements could not be obtained at low temperatures. Figure 7 shows the results to be in good agreement with those of Turner for glasses of approximately the same composition.

VI. Results

TABLE III
Soda-Silica Glasses

Glass No. 1

Viscosity °C	Viscosity Log η	Resistivity °C	Resistivity Log ρ
967	1.843	1319	$\bar{1}$.642
1176	0.949	1238	.693
1052	1.387	1154	.772
1129	1.086	1082	.824
1253	0.785	1033	.821
1108	1.240	981	.934
1360	0.541	937	.982
1273	0.703		
1169	1.004		

Glass No. 2

Viscosity °C	Viscosity Log η	Resistivity °C	Resistivity Log ρ
915	3.337	1288	$\bar{1}$.970
973	2.949	1294	$\bar{1}$.970
1088	2.387	1304	$\bar{1}$.946
1149	2.115	1275	$\bar{1}$.970
1338	1.471	1257	0.014
997	2.843	1152	.053
1257	1.718	1078	.124
946	3.208	946	.178
842	3.946	842	.361
817	4.180	817	.386
1142	2.259	1057	.139
		1043	.155

Glass No. 2

(°C)	Log resistivity	(°C)	Log resistivity
651	0.795	505	1.382
634	0.804	498	1.428
622	0.829	485	1.515
611	0.865	477	1.570
589	1.020	464	1.628
571	1.088	458	1.732
558	1.145	442	1.778
548	1.163	441	1.854
540	1.225	432	1.924
524	1.286	425	2.027
514	1.347	420	2.053

[9] (*a*) G. S. Fulcher, I, *Jour. Amer. Ceram. Soc.*, **8** [6], 339–55 (1925); II, **8** [12], 789–94 (1925). (*b*) R. F. Proctor and R. W. Douglas, *Jour. Soc. Glass Tech.*, **13**, 194 (1925). (*c*) J. T. Littleton, *ibid.*, **15**, 268 (1931). (*d*) H. R. Lillie, *Jour. Amer. Ceram. Soc.*, **12** [8], 527 (1929). (*e*) V. H. Stott, Constitution of Glass, p. 89 (1927), published by the Society of Glass Technology, W. E. S. Turner, editor.

[10] E. Seddon, E. J. Tippet, and W. E. S. Turner, "Electrical Conductivity of Sodium-Metasilicate Glasses," *Jour. Soc. Glass Tech.*, **16**, 450–77 (1932). (Measurements taken from 25 to 500°C.)

Glass No. 3

Viscosity °C	Viscosity Log η	Resistivity °C	Resistivity Log ρ
1040	3.019	1040	0.263
880	3.940	880	.528
829	4.417	829	.553
758	5.098	758	.698
1013	3.144	1013	.295
1160	2.532	1160	.186
1252	2.195	1252	.162
1318	1.940	1318	.098
1288	2.019	1288	.130
1209	2.240	1209	.176

Glass No. 3

°C	Log ρ	°C	Log ρ
940	0.431	623	1.041
865	.474	598	1.085
827	.519	586	1.147
795	.565	575	1.229
770	.642	555	1.309
743	.679	530	1.431
728	.731	520	1.519
718	.776	506	1.612
697	.821	495	1.732
671	.863	485	1.821
645	.909	465	2.011

Glass No. 4

Viscosity °C	Viscosity Log η	Resistivity °C	Resistivity Log ρ
1166	2.907	1166	0.302
1071	3.305	1071	.343
1316	2.347	1316	.192
1280	2.451	1280	.206
928	4.277	928	.545
871	4.685	871	.596
1050	3.402	821	.769
939	4.143		
1242	2.481		
814	5.163		

Glass No. 4

°C	Log ρ	°C	Log ρ
1166	0.301	564	1.805
1071	0.342	548	1.990
1316	0.192	538	2.077
1280	0.206	528	2.097
928	0.544	510	2.213
871	0.595	567	2.261
821	0.769	497	2.375
631	1.422	487	2.457
615	1.510		
576	1.741	781	0.912
563	1.821	765	0.997
581	1.721	758	0.997
615	1.510	726	1.073
		705	1.213
618	1.554	693	1.215
598	1.667	678	1.275
584	1.702	662	1.389

Glass No. 5

Viscosity °C	Viscosity Log η	Resistivity °C	Resistivity Log ρ
1280	2.819	1074	0.757
1220	3.029	1123	.675
1272	2.819	1276	.654
1262	2.895	1323	.356
1255	2.912	1285	.376
1221	3.065	1204	.503
1168	3.310		
1215	3.099		
1317	2.727		
1376	2.538		

Glass No. 7 was used as a check on the calibration of the instrument. Using the latest multiplying factor obtained with the standard glass, 6, viscosity values show excellent agreement with the values of H. R. Lillie for this glass.

Glass No. 7

Viscosity °C	Viscosity Log η	Resistivity °C	Resistivity Log ρ
824	5.084	824	1.096
742	6.197	742	1.378
737	6.282	737	1.425
747	6.125	747	1.391
1162	2.606	1162	0.420
1075	3.065	1075	0.525
848	4.800	848	1.014
1263	2.180	1263	0.221
1058	3.135	1058	0.537
971	3.703	971	0.692
950	3.879	950	0.768
839	4.921	839	1.051
1325	1.959	1315	0.237
		1324	0.261
		1260	0.285
		1240	0.342

Glass 1 BS

°C	Log η	Log ρ
1109	2.988	1.289
1203	2.575	1.245
1250	2.248	1.240
820	5.348	1.635
840	5.190	1.602
1337	1.822	1.240
980	3.743	1.373
895	4.531	1.490
815	5.424	1.675
816	5.424	1.654
913	4.406	1.444
1112	3.044	1.274
940	4.106	1.385
1180	2.561	1.253
1301	2.008	1.228
1042	3.345	1.319
732	6.835	1.954
738	6.738	1.954
734	6.776	1.954
780	6.026	1.782
1086	3.043	1.290
1197	2.424	1.245
1182	2.521	1.258
813	5.503	1.654
1166	2.600	1.261

This glass showed after one of the runs that a small amount of silica had separated out and had formed a very thin ring around the platinum crucible.

The values of viscosity for glasses 2BS, 4BS, 1LB, and 2LB were determined by H. R. Lillie. Resistances, not specific resistances, of these glasses were determined by placing about 30 grams of the glass in the platinum cylinder described above. One lead was a platinum wire fused to the side of the cylinder and the other was the platinum side of a platinum platinum-rhodium thermocouple placed in the center of the cylinder. The temperatures were measured by this thermocouple.

The glass was heated at about 1400°C until bubble-free and then cooled at a rate not exceeding 4°C per minute while measurements were being taken. This method was compared with the other method described above and the results were found to be identical.

Glass 2 BS			
°C	Log resistance	°C	Log resistance
1410	0.985	976	1.714
1346	1.058	885	1.959
1298	1.128	775	2.388
1237	1.207	672	2.959
1177	1.304	575	3.705
1075	1.480	455	4.807
Glass 4BS			
1387	0.851	830	2.140
1305	0.894	733	2.676
1225	1.043	637	3.371
1145	1.191	540	4.301
1041	1.388	440	5.455
935	1.742	390	6.112
Glass 1LB			
1390	0.585	823	1.822
1315	0.681	725	2.266
1220	0.795	622	2.932
1124	0.956	530	3.797
1015	1.214	508	4.114
925	1.449		
Glass 2LB			
1394	0.956	828	2.432
1322	1.131	735	2.927
1224	1.275	635	3.646
1115	1.515	535	4.653
1013	1.778	468	5.693
920	2.087	410	6.471

Three runs were made on glass 3BS. The glass was taken out as soon as it showed inconsistent viscosity readings. In each case there was a layer of silica, perhaps $^1/_{16}$ inch thick, on the surface of the melt. The material was identified as α cristobalite by means of X-ray photographs. The body of the melt was clear and showed no lines in the X-ray photograph. The values of viscosity given here are those of the glass when it was not devitrified. Viscosity values for the devitrified glass were on a curve considerably higher. The resistance values were not changed when the silica separated out.

Glass 3BS		
°C	Log viscosity	Log resistivity
956	4.461	1.429
1034	3.859	1.241
1100	3.475	1.112
790		1.990
792		1.952
1259	2.807	0.892
1354	2.424	0.699
1319	2.667	0.769

Glass 5BS		
°C	Log η	Log ρ
1172	2.968	1.514
1000	3.944	1.902
1094	3.386	1.647
1231	2.760	1.412
866	5.140	2.483
792	6.182	2.935
796	6.089	2.909
738	7.015	3.342
758	6.642	3.184
1354	2.345	1.374

VII. Theoretical Discussion

(Following K. Lark-Horovitz[†])

The connection between viscosity, η, and conductivity of an electrolyte is given by the equation $\lambda = \Sigma Nev$, where N is the number of charges, e the elementary charge, and v mobility. The mobility is defined as the velocity acquired under

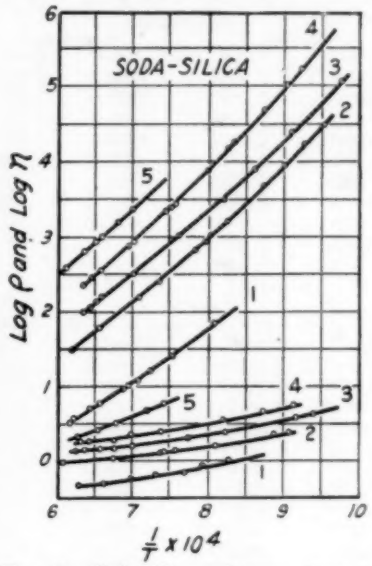

FIG. 8.—Soda-silica glasses. Log η and log ρ against $1/T$.

the force 1. From Stokes' law we have then $1 = 6\pi\eta rv$ and therefore we find for the mobility $v = {}^1/_6\,\pi\eta r$. This leads at once to the equation $= \mu\gamma$ constant, if N and the ionic radius remain constant. This rule is also known under the name of Walden[11] who first applied it to organic electrolytes.

An inspection of our log viscosity- and log resistivity-temperature curves (Figures 8, 9, and

[†] The author is indebted to K. Lark-Horovitz for the use of an unpublished manuscript given before the American Ceramic Society, February 13, 1934. Literature is also taken from this manuscript.

[11] Walden, *Z. physik. Chem.*, **55**, 246 (1906). See also Hatschek, "Viscosity of Liquids," pp. 178–79, and R. Lorenz, "Raumerfuellung und Ionenbeweglichkeit."

10), shows that log viscosity and log resistivity do not change in this way.

Plotting log η against log ρ we find that the relation of resistivity to viscosity can be represented by the formula: $\eta = \alpha\rho^{\beta}$ whereas Walden's rule would lead to a formula of the type $\eta = \rho$ constant.[12] See Figures 11 and 12. This formula holds over the whole range of temperatures which we investigated (that means between 700°C and 1400°C). For some of the commercial glasses viscosity measurements of Lillie at low temperatures were made available and the writer carried the conductivity measurements as low as about 400°C. For some of these glasses, conductivity

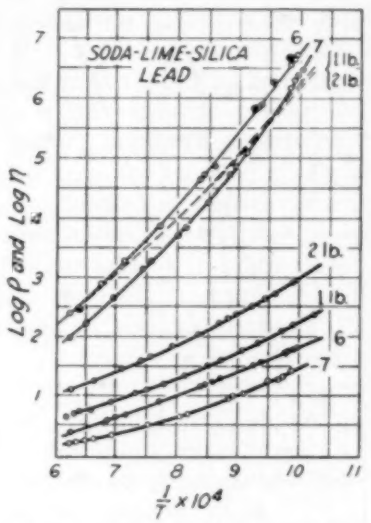

FIG. 9.—Soda-lime-silica and lead glasses. Log η and log ρ against $1/T$. (Solid dots for 6 and 7 are Lillie's values; circles are our values.)

data of W. W. Shaver were made available, which cover a still lower range. In plotting these results in a curve with those in the present paper, in the case of borosilicates, a straight line is obtained for the whole temperature range with log η against log ρ.

Recently, H. R. Lillie has carried out some more precise measurements for the two glasses 6 and 7 (notation from our table, p. 332). Plotting the log η and log ρ for these glasses, a change in slope is found near the softening point. Since, at the present time, no more viscosity data at low temperatures are available, it is impossible to say whether borosilicates in general have a different behavior from soda-lime-silica glasses. It will be of the greatest interest to have the complete viscosity data for the pure soda-silica glasses for which, through these investigations and those of Turner, the electrical conductivity is known throughout the entire temperature range from room temperature to 1400°C.

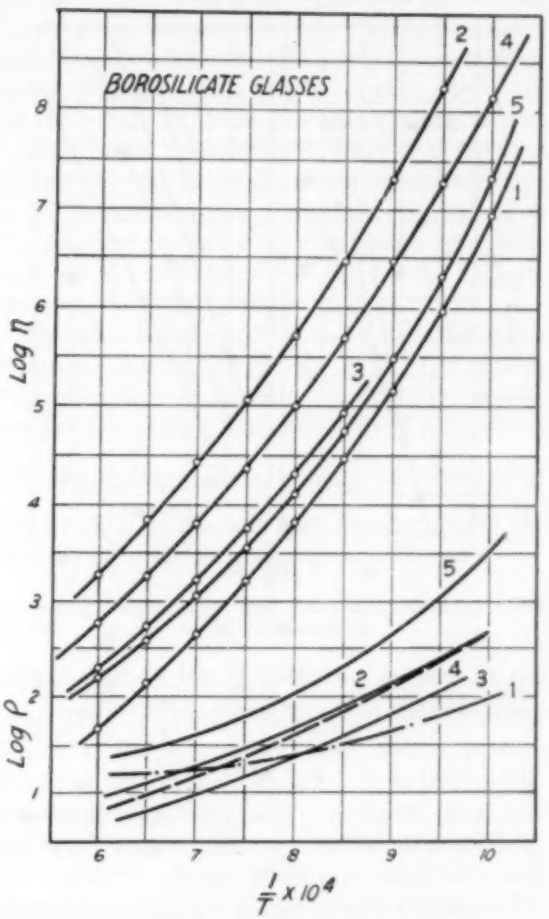

FIG. 10.—Borosilicate glasses. Log η and log ρ against $1/T$.

The formula contains two constants which change from glass to glass, and therefore, since both resistivity and viscosity are dimensioned quantities, the formula has no physical sense.[13] It is therefore useless to compare these constants for the different glasses in order to draw any conclusions regarding their change as a function

[12] This formula and the curves represented above for the glasses 6, 1LB, 2BS, 4BS were reported to the Corning Glass Works, April, 1932; *Ind. Eng. Chem.*, **25**, 753 (1933).

The electrical conductivity measurements and their connection with viscosity by the formula above were made available by K. Lark-Horovitz and C. L. Babcock.

[13] K. Lark-Horovitz and C. L. Babcock, *Phys. Rev.*, **44**, 321 (1933); also M. Reiner, *Naturwissenschaften*, **21**, 299 (1933).

of composition. It is necessary to investigate first the temperature dependency of each quantity in order to see how they are related.

Many resistivity measurements have been carried out on solid salts and glass and also on molten salts and glass as a function of temperature. By using either a thermodynamic picture (van't Hoff isotherm) and contemplating the work necessary to separate the ions of different kinds or by using a kinetic picture for the problem to find an ion either bound or free (Boltzmann principle), an expression of the form,

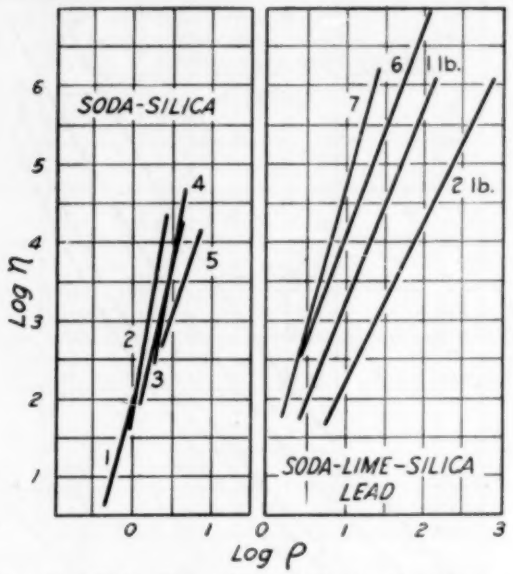

FIG. 11.—Soda-silica, soda-lime-silica, and lead glasses. Log η against log ρ.

$$\rho = \rho_0 e^{\frac{E}{kT}},$$

has been obtained. This expression has been used for solid bodies by Königsberger[14] and for glasses by Rasch and Hinrichsen.[15]

It has been found that for a wide range of temperature, this simple relation seems to hold. For temperatures near the melting point, it has been found that this formula does not represent correctly the behavior of the substance. Different ways have been chosen to interpret this deviation.

Starting with the conception of vagabonding ions in the interlattice spaces, A. Smekal[16] has proposed a formula containing two exponentials. A great number of investigators have shown that in this way some of the facts can be satisfactorily explained.[17] Another attempt was made rather early by Königsberger to account for deviations from the simple exponential by introducing additional terms to the exponential. Using the relation of Nernst-Kirchoff for the temperature dependency of chemical reaction, he proposes a formula of the type

$$\rho = \rho_0 \sqrt{\frac{T}{T_0}}\, e^{\frac{B}{K}\left(\frac{1}{T}-\frac{1}{T_0}\right) - \frac{B'}{K}(T-T_0)\left(\frac{T}{T_0}\right)^{\frac{\text{const.}}{k}}},$$

which, however, contains a great number of constants which have to be evaluated. Actually, as pointed out by K. Lark-Horovitz, it is only necessary to write the work function as $B = B' \times f(T)$.

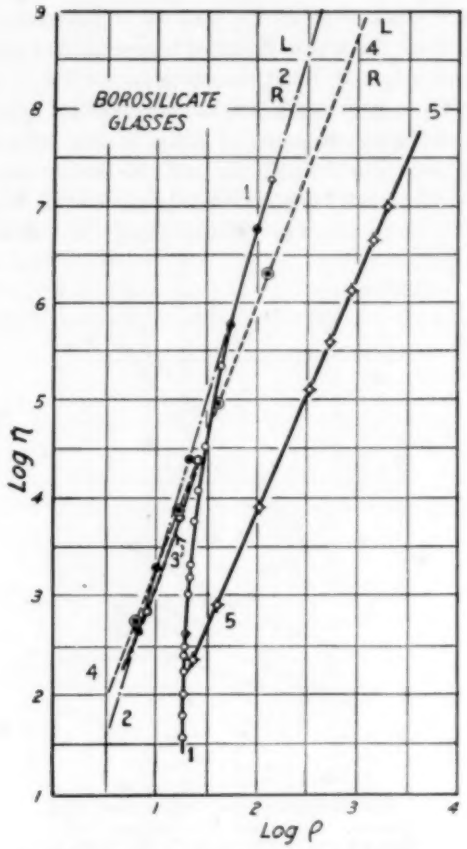

FIG. 12.—Borosilicate glasses. Log η against log ρ.

[14] J. Königsberger, *Ann. Physik*, **32**, 178–230 (1910).
[15] E. Rasch and F. W. Hinrichsen, *Z. Electrochem.*, **14** (1907).
[16] A. Smekal, *Glastech. Ber.*, **7**, 265, 386 (1929).
[17] See on the other hand the critical remarks by W. Jost, *Jour. Chem. Phys.*, **1** [7], 466–75 (1933).
For further literature on electrical conductivity, see the paper of E. Fulda, *Sprechsaal*, 1929. Also W. E. S. Turner, footnote 10. For conductivity measurements on molten salts, see R. Lorenz quoted above. See also Glastechnische Tabellen, page 283.

Similar formulas as the ones used for conductivity have also been introduced for the interpretation of viscosity for a certain range of temperature. It is possible also to represent viscosity by the equation

$$\eta = \eta_0 e^{\frac{E}{KT}}.$$

A formula of this type was first given in recent times by C. V. Raman.[18] A fact which is usually overlooked is that this formula has been in use for quite a long time.[19] In the first investigations of this type sharp breaks in the log η-temperature curves have been interpreted as different transition points.

Recent measurements with a slow rate of cooling, as well as measurements of the writer, show that such sharp breaks can not be observed. But the results in this paper, also those of Lillie for viscosity, and of Turner for resistivity, show the following features: log η and log ρ, as functions of temperature, give straight lines in the solid region. They become steeper in the softening range and then flatten out again. It is also clear that the sum of two exponentials could not explain this inflection point (see Smekal, footnote 16).

This fact, however, can be explained if one assumes that the work function is not temperature independent. Starting with the van't Hoff isotherm, it is possible in a purely formal way to write for the temperature dependency of either viscosity or resistivity, the formula

$$\eta = \frac{1}{A} e^{\frac{Bf(T)}{T}}.$$

In this formula $f(T)$ is dependent on the change of heat content by varying the temperature range of observation. In the solid crystalline state $f(T)$ will be nearly a constant and therefore it can be understood that a straight line can represent the relation between log η or log ρ and $1/T$. Since specific heat data are not available at the present time, another empirical formula has been found.

It has been shown by Fulcher[20] and Tammann[21] that viscosity in the viscous region can be represented by a formula of the type $\eta = Ae^{\frac{B}{T - T_0}}$. This has been interpreted as to indicate the range through which the glass has plastic properties. If one interprets T_0 as a "critical temperature" for which $T = T_0$, this formula presents great difficulties.

No viscosity measurements have been carried out down to a temperature equal to T_0, but the conductivity measurements by W. E. S. Turner and his associates cover this range for soda-silica glasses and do not show any break in the curve for $T = T_0$. A recent discussion of the Adams and Williamson law by G. W. Morey[22] at the Cincinnati Meeting of the American Ceramic Society seems to indicate that equilibrium conditions in the glass are reached only after such long periods that one can not decide yet whether the T_0 has a definite physical meaning.

But the meaning of the Fulcher-Tammann formula has been interpreted by K. Lark-Horovitz as giving empirically the temperature dependency of the work function $B = B'f(T)$, where $f(T) = \frac{T}{T - T_0}$. A temperature dependency of the work function has also been proposed by Waterton.[23] His formula can be written as

$$\eta = \alpha e^{\frac{B \cdot e^{\frac{T_0}{T}}}{T}}.$$

While this formula does not lead to an infinite value for $T = T_0$ like the formula above, it also, like the simple formula used above, necessitates the assumption that $T_0 = 0$ in the nonviscous region.*

The A, B, T_0 values have been calculated for the different glasses and the following table shows the corresponding constants. Good agreement has been found between experimental results and the formula.

In considering the values of the constants, it is first of all important to notice that the values of T_0 are the same for both quantities, as they have to be if the straight-line relation between log η and log ρ as expressed by the formula $\eta = \alpha\rho^\beta$ should hold. The existence of this formula simply

[18] C. V. Raman, *Nature*, **111**, 532, 600 (1923).

[19] See discussion in *ibid.*, **125**, 309, 582 (1930). For historical survey see Hatschek, *loc. cit.*, pp. 63 to 78 and L. Graetz and Karl Stoekel, Vol. 5, pages 392 to 472, Handbuch der Physikalischen und Technischen Mechanik.

[20] G. S. Fulcher, *Jour. Amer. Ceram. Soc.*, **8** [6], 339; [12], 789 (1925).

[21] G. Tammann, Aggregatzustand, Leipzig, 1922; and W. Hesse, *Z. anorg. allgem. Chem.*, **156**, 245 (1926).

[22] G. W. Morey, "The Constitution of Glass," *Jour. Amer. Ceram. Soc.*, preceding paper, this issue.

[23] S. C. Waterton, *Jour. Soc. Glass Tech.*, **16**, 250 (1932).

* For glasses 1 BS and 1, devitrification allows application of this formula for only part of the investigated range.

means that the temperature dependency of the work function for both has to be the same.

Calling $\rho_\infty = 1/A'$ and $\eta_\infty = 1/A$, the formula might be written (according to Lark-Horovitz) as

$$\left(\frac{\eta}{\eta_\infty}\right) = \left(\frac{\rho}{\rho_\infty}\right)^\beta.$$

The coefficient, β, is the ratio of the work functions

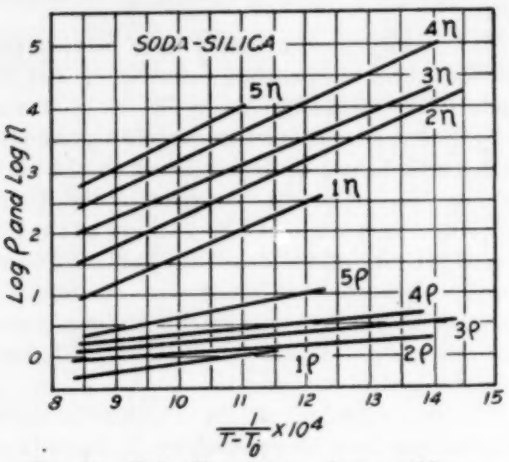

FIG. 13.—Soda-silica glasses. Log η and log ρ against $\frac{1}{T - T_0}$.

of viscosity and resistivity, whereas the quantities $1/A$ are the viscosities or resistivities at infinitely high temperature. There is no objection to this formula on dimensional grounds.

For the present results, the work function for viscosity is found to be many times greater than

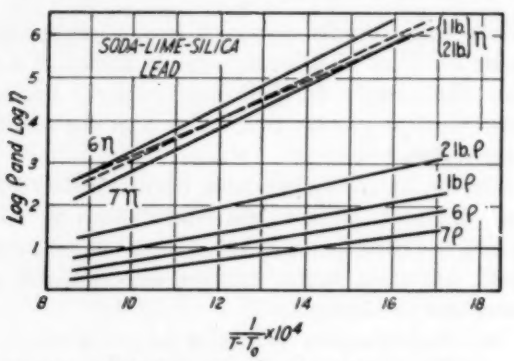

FIG. 14.—Soda-lime-silica and lead glasses. Log η and log ρ against $\frac{1}{T - T_0}$.

the one for resistivity. By analyzing the known data on molten salts, Lark-Horovitz has found that this holds also for salts and for solutions of self-dissociating electrolytes, such as glycerin. The constant B can not be compared directly with the work function ordinarily used, since it is a coefficient in a form containing $\frac{1}{T - T_0}$ instead of $1/T$.

In the case of molten salts, the work function for viscosity is of the order of magnitude of a heat

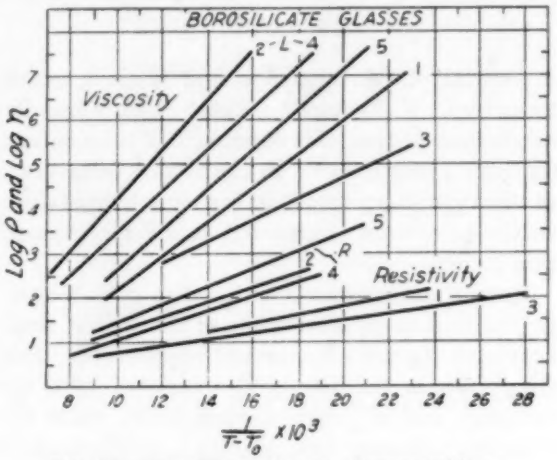

FIG. 15.—Borosilicate glasses. Log η and log ρ against $\frac{1}{T - T_0}$.

of melting. In accordance with modern theoretical considerations,[24] one would expect that the work function for conductivity should be the same or even larger than the one for viscosity. Experiments, however, show that just the opposite is true. One might explain this fact by as-

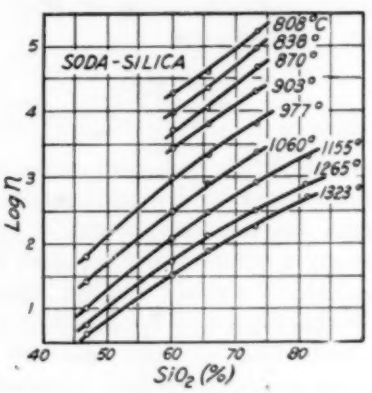

FIG. 16.—Soda-silica glasses. Log η against PCT SiO_2.

suming that the dissociation decreases with increasing temperature. However, experiments by Joffé[25] have shown, in the case of quartz, that the dissociation increases with increasing temperature,

[24] Frenkel, *Z. Physik.*, **35**, 664 (1926).

[25] A. L. Joffé, *Ann. Phys.*, **72**, 461–500 (1923) (especially pp. 480–87).

and that there is no reason to assume the opposite for glass melts. It is therefore concluded that the process of conduction is determined chiefly by the motion of the vagabonding ions through the "liquid" interstices, and the viscosity is determined by a quasi-solid network and its ramifications. This seems to be in agreement with the explanations for viscosity which are derived on the basis of X-ray investigations of liquids.[26]

table with the exception of the borate glasses 3BS and 4BS.

The $\rho\infty$ values show a maximum for glass 3, 65% silica, and become small again with increasing silica content, indicating definitely that the process of conductivity can not be a simple function of the viscosity. It is to be expected that in the lead glasses $\rho\infty$ would reach higher values than in the pure soda-silica glasses.* The higher lead

TABLE IV

Glass	Viscosity				Resistivity				
	$-\log A$	$\eta\infty$	B	T_0	$-\log A'$	$\rho\infty$	B'	T_0	β
1	2.496	0.00319	9210	302	1.340	0.04570	2820	300	3.27
2	2.075	.00841	9899	400	0.585	.26001	1527	400	6.48
3	1.614	.02432	9671	400	0.500	.31625	1612	400	6.00
4	1.588	.02582	10720	400	0.534	.29398	1989	400	5.39
5	1.339	.04581	11053	401	1.181	.06592	4230	400	2.61
6	2.062	.00867	12100	407	1.106	.07837	4085	410	2.96
7	2.430	.00371	11909	410	0.980	.10471	3244	410	3.67
1BS	1.566	.02746	8658	550	−0.085	1.21654	1969	550	4.40
2BS	1.479	.03319	13033	467	0.349	.44783	3719	465	3.50
3BS	0.070	.85106	5496	700	0.000	1.00000	1704	697	3.23
4BS	1.267	.05408	10815	500	0.544	.28571	3684	500	2.94
5BS	2.030	.00933	10569	503	0.660	.21877	4605	495	2.30
1LB	1.445	.03589	10617	399	0.942	.11428	4391	400	2.42
2LB	1.417	.03828	10617	399	0.833	.14688	5284	400	2.01

It is particularly interesting to compare the results for the soda-silicate glasses as a function of composition. Increasing silica content increases the work function for viscosity. The work function for conductivity, however, reaches a minimum for a silica content of 60% silica, and increases steadily for increasing silica content. The values of $\eta\infty$ increase with increasing silica content as one might expect, and for the largest, 81% silica, is larger than any other value in the

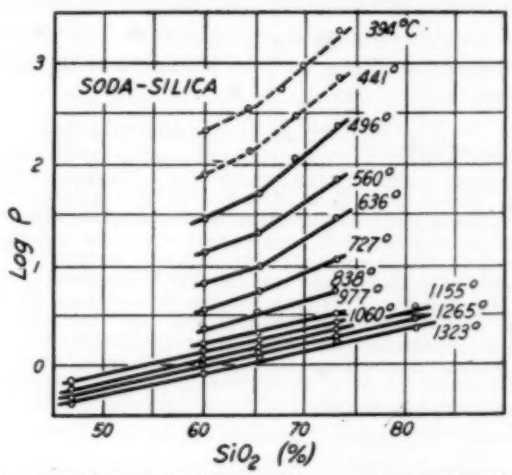

FIG. 17.—Soda-silica glasses. Log η against PCT SiO_2.

content also corresponds to a greater work function of conductivity, whereas the work function for viscosity is unchanged.

It is rather surprising to find that the value of $\rho\infty$ for all of the borate glasses is much higher[27] than for any other glasses, especially so, since some of these glasses are comparatively good conductors at low temperatures.

It is known from the work of Gehlhoff that the mixture of potassium and sodium reduces the conductivity. The glass 5BS containing 10% K_2O has the highest work function of all the glasses of the borate group, possibly due to the formation of complexes, but its $\rho\infty$ is smaller than any of the others.** The silica content of this glass is only 56%, the smallest content of the whole borate glass group. If the glasses of this group are arranged with increasing silica content, it is found that the glass with the highest silica content (2BS) also has the highest work function for viscosity, but the work function for all the glasses compared as a function of SiO_2 content, goes through a minimum and increases again for higher values. The values of $\eta\infty$ have a maxi-

[26] G. W. Stewart, *Phys. Rev.*, **38**, 1575–82 (1931).

* The $\rho\infty$ given here can not be taken in direct comparison, since no specific resistances have been measured, and the rate is quite arbitrary. The same holds for 4BS and 2BS.

** Investigation of glasses of the potassium sodium silica group have shown that the addition of potassium in excess of sodium produces new and complex phenomena.

mum at the same point where the values for the work function have a minimum. The corresponding values for conductivity show an entirely different behavior and no such pronounced regularity, but also in this case the values for ρ_∞ first increase with increasing silica content and then fall off again.* The work functions for conductivity show a minimum at the same point where the work functions of viscosity show it, but the glass with the highest silica content contains only sodium ions and a small amount of alumina has a smaller work function than the glass with the smallest silica content, the same percentage of sodium, but 20% BaO and 10% K_2O. It will be necessary to have a larger number of systematically varied borate glasses to draw any definite conclusions regarding the distribution and the binding of the ions in these glasses.**

VIII. Summary

(1) An instrument has been constructed which permits simultaneous measurements of electrical resistivity and viscosity.

(2) A number of commercial borate glasses, some soda-lime-silica glasses, lead glasses, and five soda-silica glasses have been investigated through the viscous region, 700 to 1400°C, for both viscosity and electrical resistivity. Electrical resistivity measurements have been carried out beyond this range down to about 400°C. For glasses of comparable composition the results are in excellent agreement with those obtained by W. E. S. Turner, who used an entirely different method.

(3) The relation between viscosity and electrical resistivity for all these glasses can be represented by a formula of the type $\eta = \alpha\rho^\beta$. For two glasses, for which precise low temperature viscosity and resistivity measurements were available, it has been found that this relation does not hold below the viscous range. As far as preliminary experiments show, it seems to hold over the whole range of observation for some borate glasses.

(4) The temperature dependency of both viscosity and resistivity can not be represented by a simple relation like $\log m \sim 1/T$. Plotting $\log \eta$ or $\log \rho$ as a function of $1/T$, smooth curves are obtained throughout the whole range.

(5) According to Lark-Horovitz, the work function in the viscous range has to be assumed as a function of temperature:

$$\left.\begin{matrix}\eta \\ \rho\end{matrix}\right\} = Ae^{\frac{Bf(T)}{T}}$$

and

$$B = B_0\frac{T}{T - T_0}.$$

This formula leads to the expression

$$\left(\frac{\eta}{\eta_\infty}\right) = \left(\frac{\rho}{\rho_\infty}\right)^\beta$$

where $\beta = \dfrac{B \text{ viscosity}}{B' \text{ resistivity}}$.

(6) In all cases the work function for viscosity is found to be several times greater than that for resistivity, indicating that the resistivity depends not only on the viscosity, but the binding forces of the ions as determined by the chemical composition of the glasses and the structure of the glass itself.

Acknowledgments The author expresses indebtedness to The Corning Glass Works, who made this work possible by the creation of a Fellowship at Purdue. He is under great obligation to K. Lark-Horovitz, who first outlined this problem and under whose direction this investigation has been carried out. He wishes to thank G. W. Sherman, Jr., for assistance in some of the high-temperature measurements. He is indebted to A. I. May and Wm. J. Holden, Purdue Physics Shop, for the fine craftsmanship in building the new instruments. Finally, the author wishes to express appreciation to J. V. Hoffacker, first holder of the Corning Fellowship, who constructed the torque measuring instrument and made other important contributions to the investigation.

** Such investigations are under way now. In the meantime K. Lark-Horovitz and C. K. Stedman have started investigations using high frequency currents so as to find a possible explanation based on the theory of strong electrolytes.

VISCOSITY AND REBOILING OF BLUE GROUND COATS*

By R. R. Danielson and J. D. Tetrick

ABSTRACT

The evolution of gases during the firing or refiring of ground coats on sheet iron or steel may be the cause of certain types of copperheading in the ground coat or in blistering of the cover enamel. The fluidity of the ground coat in the melted state on the ware has an important bearing on its ability to free itself of the gases.

The calculated refractory value of an enamel is an index of its fusibility and fluidity during the firing operations. It is therefore an aid in the compounding of enamels which will minimize the defects arising from the evolution of gases during the firing of the enamels.

I. Introduction

Reboiling may be defined as that evolution of gas which occurs when ground coats on sheet iron and steel are reheated to enameling temperatures subsequent to their initial firing. The gases apparently originate in the metal base or in some reaction between the base and enamel. This problem of reboiling will undoubtedly continue under the present commercial methods for producing sheet enameling stock. The manufacture of enamels which will minimize the effects of reboiling is therefore essential. Schaal[1] has called attention to the beneficial effects of additions of a fusible glass to the ordinary ground coats in relieving the defects caused by the evolution of these gases. Granting that the fusibility of the enamel is an important factor in the effects of reboiling, the enameler is interested in specific information which will assist him in developing such enamels.

It is believed that the tools are at hand in the method given by Staley[2] for calculating what he has termed the "refractory value" of ground coats for cast iron. This refractory value is the ratio of refractories to fluxes and gives an index of the fusibility of an enamel. It has been used to advantage in developing various types of enamels of desired fusibility without resorting to elaborate tests for determining the fusibility of individual compositions.

II. Experimental

For the purpose of these experiments, five ground coats of various refractory values were selected from a series of ground coats which had been studied. These are given in Table I with their fusibility properties indicated. The batch compositions are shown in Table II.

As an example of the method employed in calculating the "refractory value," the following procedure shows the essential steps in the calculations on Enamel D, shown in Table I. It is necessary to calculate the oxide constituents of the enamel from the raw batch materials. The various oxides are then multiplied by arbitrary factors which express their relative refractory or fluxing effects on the enamel. It has been found by experiment that the following factors for the several oxides give comparable results: SiO_2 1.0, Al_2O_3 3.0, Na_2O and K_2O 2.0, B_2O_3 1.0, CaF_2 1.0, metallic oxides 1.0.

These enamels were smelted under commercial conditions and were ground to the usual fineness for application by draining. Mill batches consisted of 100 frit, 7 Johnson Porter "B" clay, 0.25 magnesium carbonate, 0.25 borax, and 50 water. The ground coats were applied to 7- by 10-inch, 20-gage, ingot iron plates obtained from regular stock of an enameling plant. Suitable firing temperature and time as noted in Table I for the individual ground coats were determined by trial.

III. Discussion of Results

(1) Boiling During Firing of Ground Coats

In firing the ground coats observations were made to note the condition of the enamel surface during the firing cycle. On all trials there was the characteristic boiling action which started about 50 seconds after the plates were placed in the furnace. This boiling continued for approximately 25 seconds and there was no apparent relation between enamel composition and time over which

* Presented at the Annual Meeting, American Ceramic Society, Cincinnati, Ohio, February, 1934 (Enamel Division). Received March 13, 1934.

[1] (*a*) R. B. Schaal, "A Discussion of Plant Problems," *Jour. Amer. Ceram. Soc.*, **15** [9], 410–14 (1932). (*b*) R. B. Schaal and D. H. Fuller, "Modern Enameling Troubles," *Ceram. Ind.*, **15** [6], 612 (1930).

[2] H. F. Staley, "Principles of Enameling," *Ceramist*, **6**, 384 (1925).

the boiling continued. There was, however, a decided difference in the manner in which the gas was given off. With enamels of low refractory value, the gas bubbles were relatively more numerous and fine. In the case of the high refractory-value enamels, the gas bubbles were not so numerous but were much larger in size. This condition is such in the case of Enamel E that large holes opened up directly to the iron base. The viscosity of the enamel was so great that the bubbles remained open allowing the exposed metal to become oxidized and form large copper-heads.

TABLE I

ENAMEL COMPOSITIONS AND PROPERTIES

Enamel	Oxide composition for 100 lb. melted glass calculated: SiO_2	Al_2O_3	$Na_2O + K_2O$	B_2O_3	CaF_2	Metal oxides	Refractory value	Flow on fusion block (notches)	Firing data: Temp. (°F)	Time (min.)
A	50.1		17.9	21.6	7.4	3.0	0.74	6+	1590	3
B	40.6	7.4	20.0	16.5	13.1	2.4	0.87	5	1590	3½
C	45.0	6.7	19.4	17.0	9.5	2.4	0.96	4+	1590	4
D	49.2	6.0	18.9	17.5	6.0	2.4	1.06	3	1590	4½
E	47.6	8.0	19.0	14.0	9.0	2.4	1.13	2	1590	5

ENAMEL D: CALCULATION OF REFRACTORY VALUE

	(%)		(%)	(%)
Flint	28.1	SiO_2	28.1	49.2
		SiO_2	21.1	
Feldspar	31.5	Al_2O_3	6.0	6.0
		$Na_2O + K_2O$	4.41	
Sodium nitrate	4.0	Na_2O	1.46	18.9
Soda ash	9.2	Na_2O	5.32	
Borax	47.7	Na_2O	7.71	
		B_2O_3	17.5	17.5
Fluorspar	6.0	CaF_2	6.0	6.0
Metallic oxide	2.4	Metal oxides	2.4	2.4
				100.0

Refractories		Fluxes	
SiO_2	$49.2 \times 1 = 49.2$	$Na_2O + K_2O$	$18.9 \times 2 = 37.8$
Al_2O_3	$6.0 \times 3 = 18.0$	B_2O_3	$17.5 \times 1 = 17.5$
	67.2	CaF_2	$6.0 \times 1 = 6.0$
		Metal oxides	$2.4 \times 1 = 2.4$
			63.7

Refractory value: $\frac{67.2}{63.7} = 1.06$

(2) Reboiling of Fired Ground Coats

The ground-coated plates were aged after firing for 48 hours, when they were given a reboiling test. This was accomplished by placing the plates in a furnace heated to 1500° and observing the surface of the ground coat during a period of about 90 seconds which is the time for normal firing of a white cover coat under the conditions of this firing.

During this firing period the usual reboiling phenomenon occurred. Approximately 40 seconds after the plates were placed in the furnace there was an evolution of gas from the ground-coat surface which continued for about 25 seconds. As in the firing of the ground coats, the bubbles were smaller but more numerous in the case of the enamels with the lower refractory value and larger but less numerous in the case of the enamels with high refractory value. The time for reboiling was practically the same for the five enamels which were used in these experiments.

In order to show definitely the effects of this reboiling on white cover coats, the reboiling tests were repeated on the ground-coated plates over which a coat of white enamel had been applied. The tests were made on plates heated for 45, 60, and 75 seconds at a temperature of 1500°F. All ground coats reboiled after the plates had been in the furnace for 40 seconds.

TABLE II

BATCH COMPOSITION

Enamel	Feldspar*	Flint	Borax	Soda niter	Soda ash	Fluorspar	Metallic oxides
A		50.1	59.0	3.5	12.2	7.4	3.0
B	39.0	14.5	45.0	3.5	10.3	13.1	2.4
C	35.2	21.5	46.4	3.5	8.9	9.5	2.4
D	31.6	28.0	47.7	3.5	9.5	6.0	2.4
E	42.0	19.5	38.2	3.5	9.5	9.0	2.4

* Feldspar: 67% SiO_2, 19% Al_2O_3, 14% $Na_2O + K_2O$.

The plates reheated 45 seconds just began to show indications of the fusing of the cover enamel. The bubbles were very numerous but small in size on the ground coats of lower refractory value and smaller in number but of large size in the more refractory compositions.

The plates reheated 60 seconds showed the cover

coat glazed over but still somewhat immature. The small blisters had practically disappeared in the white enamel applied over the ground coats of low refractory value but were still prominent as raised bubbles in the refractory enamels.

On the plates reheated 75 seconds, the cover enamel had flowed to a smooth finish. Enamel E was the only ground coat which had not developed a smooth finish. It showed evidence of trapped gases and the copperheads opened up.

(3) Fusibility of Ground Coats In order to determine the fluidity of the ground coats, tests were made by means of the so-called fusion test blocks. The results are shown in Table I and the close relationship existing between refractory value, required firing time, and fluidity of the enamels as indicated by the fusion block test is marked.

The work of Harrison and Sweo[3] on the fusion properties of ground-coat enamels gives a further opportunity to check the relationship between the refractory value and the fusibility of normal enamels. The excellent correlation existing between the refractory value, as calculated from the theoretical composition and the fusibility of these enamels as actually determined by test, is shown in Table III.

It is expected that the importance of the refractory value will be limited to enamels within the range of normal enamels. For example, enamels with excessive amounts of sodium oxide are extremely viscous due to the precipitation of soda compounds which cannot combine with the other glass-forming constituents. The calculated refractory value for such an enamel, while very low, would obviously have no significance.

TABLE III

RELATIONSHIP OF REFRACTORY VALUE AND FUSIBILITY

Ground-coat* enamel	Calculated refractory value	Cone deformation* (temp. °F)	Fusion block test* "finish" (temp. °F)
A	1.01	1191	1359
B	1.06	1247	1418
C	1.11	1279	1470
D	1.02	1209	1368
E	1.07	1256	1429
F	1.12	1294	1481
G	1.03	1222	1386
H	1.08	1265	1445
I	1.13	1301	1497

* See footnote 3.

In addition to the fusibility of enamels there are many other important factors which must be considered. Among these are firing range, expansivity, strength, and other properties. For this reason the combination of several frits to obtain required properties has become a common and desirable practice. Some of the compositions used in this study would find best application in that way.

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[3] W. N. Harrison and B. J. Sweo, "Some Fusion Properties of Ground-Coat Enamels as Influenced by Composition," reprinted from *Bur. Stand. Jour. Research*, **10**, 191 (1933).

FURTHER DATA ON REBOILING OF SHEET-IRON GROUND-COAT ENAMELS*

By A. I. Andrews and R. E. Mullady

ABSTRACT

The reported characteristics of the reboiling phenomenon have been checked and additional data which influence reboiling have been obtained.

I. Introduction

The literature is not reviewed, since it has already been adequately summarized by Lord.[1] The early part of this investigation consisted chiefly in the checking of the results of other investigations. The latter part and that described in this paper consist of new experiments which, although not conclusive, offer many new viewpoints on the theories of reboiling.

II. Enamel Batch and Preparation

The following typical ground-coat enamel was used in the general investigation:

	Parts		Parts
Feldspar	30	Fluorspar	7
Borax	30	Soda niter	3
Quartz	20	Cobalt oxide	0.5
Soda ash	8	Manganese dioxide	1.5

The enamel was made in a 60-pound batch, mixed dry, and smelted at 2100°F for 70 minutes in a rotary gas-fired smelter. After being quenched and dried, the frit was ground to pass an 80-mesh sieve. A mill batch as follows was used and the enamel was milled to such a fineness that 7 to 10% was retained on a No. 200 sieve.

	Parts
Frit	100
Clay	6
Borax	0.5
Water	42.0

III. Preparation of the Base Metal

The following preparation was used on all iron except the stainless steel. The pieces of metal were first cleaned in a boiling solution of alkali cleaner. After the metal was thoroughly clean, the pieces were rinsed in hot water and then pickled in a 5% solution of sulfuric acid at a temperature ranging from 150 to 160°F. The pickling was followed with a hot water rinse and the process was finished by placing the specimens in a neutralizing bath of 0.5% solution of sodium carbonate at 190°F.

(1) Sandblasting The sandblasting was done with commercial sandblast sand in an induction-type sandblast machine. The specimens were blasted to roughen the surface and remove all dirt and grease.

IV. Effect of Furnace Atmosphere on Reboiling

The furnace used was of the type described by Andrews and Hertzel in their investigation of the effects of gases upon the fired properties of enamels.[2] The nitrogen was passed through a calcium-chloride tower before entering the firing chamber so it would be free from moisture. Samples of gas were taken from the immediate vicinity of the specimen and analyzed. The rate of flow of the gas through the furnace was regulated so that the atmosphere in the furnace was 100% nitrogen.

The specimens that were fired in nitrogen had a pale blue color, a ruffled surface, and contained very few bubbles. The surface of the steel at the interface seemed to be oxidized very little if at all. The enamel had poor adherence. Specimens sandblasted before enameling had somewhat better adherence than those that were pickled.

Specimens that were refired in nitrogen did not reboil.

Several specimens were refired in air after being fired in nitrogen; these samples did not reboil; however, the specimens that were fired originally in air and refired in nitrogen did reboil.

A few specimens that were fired in nitrogen were refired in air for the entire firing period. These specimens showed no improvement in bond and no increase in bubble content; when refired, they did not reboil.

V. Effect of Different Base Metals

Specimens of various iron-chromium-nickel alloys were used in reboiling tests.

The following table shows the properties and compositions of these alloys.

* Presented at the Annual Meeting, American Ceramic Society, Cincinnati, Ohio, February, 1934 (Enamel Division). Received February 21, 1934.

[1] J. O. Lord, "Summary of Observations and Facts Concerning the Phenomenon of Reboiling," *Jour. Amer. Ceram. Soc.*, **16** [9], 442 (1933).

[2] *Univ. of Ill. Eng. Expt. Sta. Bull.*, No. 214.

Number	Name	Composition	Temp. (°C)	Coefficient of expansion ($\times 10^{-6}$)
1	USS 18–8	18 Cr	100	17.2
		8 Ni	500	20.2
2	USS 25–12	25 Cr	100	16.2
		12 Ni	500	19.5
3	USS 17	17 Cr	100	11.2
			500	13.2
4	USS 27	25–30 Cr	100	10.7
			500	12.4

In preparation for enameling, specimens of the above alloys were sandblasted because such steels are difficult to pickle. The enamel was sprayed and fired at the usual temperature. After cooling, the specimens were tested for reboiling with the following results.

Numbers 1 and 2 (USS 18–8 and USS 25–12) showed no tendency to reboil.

Numbers 3 and 4 (USS 17 and USS 27) reboiled.

The bonds with Nos. 2, 3, and 4 were somewhat better than the bond obtained with No. 1.

The enamel fired down smoothly in every case.

VI. Effect of Thickness of the Base Metal

Statements in the literature indicated that the tendency toward reboiling decreased as the thickness of the metal decreased. After some preliminary work was done with regular 20-gage enameling iron and other $^1/_8$-inch and $^1/_4$-inch stock, it was decided that this statement was not exactly true.

Commercial enameling iron in various thicknesses was obtained. These were pickled, enameled, and fired properly.

The following table gives the thickness covered:

Stock No.	Gage	Thickness (in.)
2	25	0.018
3	21	0.028
4	19	0.036
5	17	0.045
6	16	0.041
7	9	0.114
8	6	0.162
9	2	0.257

After enameling and refiring to the proper temperature, the specimens from Nos. 2 to 7, inclusive, reboiled, but Nos. 8 and 9 did not reboil.

The specimens of thicker stock cooled much slower than the thinner stock. The enamel on the thicker stock was solid before the metal had cooled below red heat. In this way, the enamel received considerable annealing treatment.

Several specimens having a thickness of 0.162 inch were machined to the following thicknesses: 0.117, 0.122, 0.126, 0.132, 0.135, 0.142, 0.147, 0.152, and 0.157 inch. This group of specimens covered the range between the specimens that did reboil and those that did not.

The above specimens were enameled and tested for reboiling. All of the specimens except the one with a thickness of 0.157 inch showed a great tendency to reboil. The last specimen reboiled slightly.

VII. Effect of the Cooling Rate after Initial Firing

Several specimens were enameled and allowed to cool with the furnace from 1600°F to room temperature.

Two of the specimens were tested for reboiling immediately, while two were held for a day and then tested. Neither the specimens which were tested immediately nor those held showed any tendency to reboil.

It was decided that some specimens should be cooled rapidly to some temperature below red heat and then allowed to cool to room temperature, and the effect upon the reboiling tendencies of the enamel be noted.

To cool the specimens rapidly to a definite temperature, a bath of pure sodium nitrate was maintained at a temperature of 850°F; the specimens were enameled at 1600°F, removed from the furnace, and immediately plunged into the molten salt. The specimens cooled to the temperature of the bath within a few seconds. The specimens were then removed from the sodium nitrate and allowed to cool to room temperature in the air. The experiment was repeated with the temperature of the salt at 650°F.

All of the above specimens were tested for reboiling, and all showed the maximum tendency toward the phenomenon.

Several specimens were enameled and allowed to cool with the furnace to temperatures of 500°F, 400°F, and 300°F. Specimens were removed at these respective temperatures and allowed to cool in the air to room temperature. These specimens were held for two days and tested. The specimens removed from the furnace at 500°F showed a slight tendency to reboil. The other specimens showed no tendency toward the defect.

Although these specimens did not reboil after the above treatment, a second reheating caused reboiling. This shows that the phenomenon of cooling is closely related to reboiling.

The results of the above tests showed that by controlling the cooling rate through a proper range reboiling could be prevented in the subsequent firing period.

Another test was made in which the specimens were allowed to cool rapidly in air to a definite temperature, placed in a furnace at this temperature, and allowed to cool with the furnace.

The procedure was as follows: Two furnaces were used, the enameling furnace at 1600°F and another furnace at 650°F. A specimen was fired and allowed to cool in the air to approximately 650°F, placed in the second furnace, and allowed to cool with it. When the furnace had cooled to 350°F, other specimens were fired and placed in it and also one at 250°F. After the furnace reached room temperature and the specimens were held for two days, they were tested for reboiling. The specimens placed in the furnace at 650°F and 350°F did not reboil. The other specimens, placed in the furnace at 250°F, reboiled.

VIII. Effect of Stressing the Base Metal Prior to Enameling

From some preliminary work the theory was advanced that tension on the steel specimen may have some effect upon the reboiling characteristics of the metal.

Four specimens of Armco stock, 10 inches long and 1 inch wide, were treated in the following manner before being enameled:

Specimen	Treatment
1	Stressed to about one-half the yield-point
2	Stressed to the yield-point and held for a few minutes
3	Stressed to a value just below the ultimate; this specimen stretched approximately $^3/_4$ in.
4	Stressed until it failed

These specimens were enameled and allowed to cool in the open air; when refired the samples reboiled and no difference could be noted from the regular metal.

IX. Classification of Results

(1) The reboiling characteristics changed with chemical composition of the base metal. (*a*) Alloys Nos. 1 and 2 did not reboil; these base metals were high in both chromium and nickel. (*b*) Numbers 3 and 4 did reboil; these base metals were high in chromium, but contained no nickel.

(2) Subjecting the metal to a load either below or in excess of the yield-point or elastic limit did not affect the reboiling tendency of the metal.

(3) Reboiling decreased when the thickness of the base metal was increased. This decrease takes place over a short range. With the enamel used in this investigation, the thickness of the enameling steel above which reboiling did not occur and below which it did, was approximately 0.160 inch.

(4) With a given enamel, the reboiling tendency decreased as the thermal coefficient of expansion of the base metal increased. Enameling steel has a coefficient of approximately 10–12 $\times$ 10^{-6}. The two alloys that reboiled had a coefficient of approximately 12 $\times$ 10^{-6}, while those two that did not reboil had a coefficient from 16 to 20 $\times$ 10^{-6}.

(5) No work was done that gave definite information concerning the chemical reaction that takes place between enamel and steel. By changing the atmosphere of the furnace, the reaction between steel and enamel was changed. This was shown when the specimens were fired in an atmosphere of nitrogen. (See result No. 6.)

(6) Specimens fired in an atmosphere of nitrogen gave the following results: (*a*) they did not reboil when refired in nitrogen; (*b*) they did not reboil when refired in air; (*c*) the enamel contained very few bubbles; (*d*) the bond between enamel and steel was very poor; and (*e*) sandblasting improved the bond slightly.

(7) Specimens fired in air and refired in nitrogen showed the usual reboiling tendencies.

(8) Specimens fired initially in nitrogen and then refired in air gave the following results: (*a*) they did not reboil; (*b*) the bond was not improved by refiring in air; and (*c*) the bubble content was not increased by refiring in air.

(9) Specimens cooled with the furnace used in this investigation did not reboil.

(10) Specimens cooled with the furnace to a temperature below 500°F and removed and allowed to cool in air did not reboil.

(11) Specimens cooled rapidly to 650° by quenching in molten sodium nitrate and then allowed to cool to room temperature in the open air reboiled.

(12) Specimens removed from the furnace after enameling at 1600°F and placed in another furnace gave the following results: (*a*) those placed in the second furnace at 625° and 350° did not reboil; and (*b*) those placed in the second furnace at 250° showed a tendency toward reboiling.

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A STUDY OF WHITE GROUND COATS*

By James D. Tetrick

ABSTRACT

Strong and uniform adherence in white ground-coat enamels can be promoted through special preparation of the enameling stock either through a plating operation or by deep etching the surface. The results obtained depend upon uniformity of the preparation of the base metal and the composition of the ground-coat enamels used.

It is necessary to compound the white ground-coat enamel with considerable amounts of the accessory opacifiers in order to build up satisfactory opacity. Additions of opacifiers to the mill are also necessary. Fluidity of the enamel is important and should be high to decrease reboiling and to produce a smooth finish coat on etched stock. Addition of antimony trioxide to the raw batch of the enamel promotes adherence but develops reboiling.

I. Introduction

The primary function of any ground-coat enamel for sheet iron is to form a base coat of enamel which adheres strongly and uniformly to the metal base and over which subsequent coats of enamel may be satisfactorily applied. This function is well fulfilled by the regular cobalt blue ground coat. However, the use of such ground coats produces a base enamel of such dark color that the production of high-quality ware calls for the application of two coats of finish enamel. Thus the development of a satisfactory light colored or white ground-coat enamel would be a step forward in the technology of sheet-iron enameling.

The underlying problem is to produce in a white base enamel that strong and uniform adherence that is the prime requisite of any good ground-coat enamel. In the course of some experiments conducted in our laboratory several years ago, it was definitely shown that, if cobalt is electroplated on a sheet of iron enameling stock and this cobalt-plated metal is coated with a white base enamel, fully as good adherence is developed as in a regular cobalt blue ground coat. However, in firing the white ground-coat enamel over such a cobalt plate, a sufficient amount of cobalt is dissolved by the enamel to impart a blue color to it, and for that reason the experiments were discontinued at that time. "Nickel dips" are widely used in the grayware enamel industry for the purpose of promoting adherence.

This investigation resolved itself into three phases: (1) the search for, and investigation of, types of plating which, applied previous to the enameling operations, would produce satisfactory adherence and permit the use of white ground coats; (2) the search for some chemical means of producing a surface structure on the sheet iron to which a white ground-coat enamel would adhere satisfactorily; and (3) the development of satisfactory white ground-coat compositions.

II. Experimental

(1) The Ground Coat

During the course of the experiments, a considerable number of white ground-coat compositions were investigated. For the purpose of this paper it is not necessary to go into all of them. The group of enamel compositions as presented by melted weights in Table I was selected as the most representative. Enamel No. 1 is a regular cobalt blue ground coat with the metallic oxide addition omitted.

Table I

Melted Weights of White Ground-Coat Enamels

	1	7	14	17	21	28	33
Feldspar	31.5	10.2	10.5	10.5	10.4	10.5	10.5
SiO_2	28.1	41.1	39.5	39.5	39.1	34.8	33.8
B_2O_3	17.5	17.0	17.5	13.5	13.4	13.5	13.5
Na_2O	14.5	15.7	17.4	17.4	17.2	14.4	14.4
CaF_2	8.4	8.2	11.8	11.8	11.7	3.0	3.0
Na_3AlF_6				4.0	3.9	8.8	8.8
$Ca_3(PO_4)_2$			3.3	3.3	3.3	3.0	3.0
BaO						12.0	12.0
Sb_2O_3					1.0		1.0
Sodium antimonate		7.8					
	100.0	100.0	100.0	100.0	100.0	100.0	100.0

The enamels were milled in 10-pound lots to a fineness of 7 to 9 grams residue by the standard test. The mill additions were 6% clay, 0.25% magnesium carbonate, 0.25% boric acid, and 55% water. Where additions of opacifier were also made to the mill it will be noted in the presentation of results. Preliminary trials were made with a regular commercial white cover enamel, milled with 6% clay and 6% tin oxide unless otherwise stated.

For preliminary trials, 2- by 7-inch plates of 20-gage ingot iron were used. For the more extensive follow-up work in the fields which looked

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most promising, 7- by 10-inch plates of the same iron were used.

(2) The Metal Preparation of the metal for plating followed the commercial practice in cleaning and pickling through the boiling rinse following the pickling operation whence the plates either were transferred directly to the plating bath or were dried previous to the plating operation as convenience dictated. This variation in treatment did not vary the results. For the pickling operation, 8% sulfuric acid at a temperature of 140°F was used. A few trials were made using hydrochloric acid for pickling but this did not vary the results. Following the plating bath, the plates were given two rinses of hot water and then a boiling rinse of very weak soda-ash solution. Plating was conducted in solutions at room temperature unless otherwise noted. Pickling treatment during the course of the etching experiments will be given with the results of the etching trials.

(3) Application of Ground Coat Application of the white ground-coat enamels to the steel was made by draining. The weight of the fired ground-coat enamel was 30 grams on a 7- by 10-inch plate. The plates were finished with a single coat of regular white cover enamel weighing 18 grams, fired weight. The firing time and temperature of No. 1 ground coat was two minutes at 1580°F. The other ground coats were fired at 1520°F for a period of two minutes.

(4) Adherence Tests Adherence was judged by bending the plates sharply through 90° and by an impact test which consisted of dropping a one-inch steel ball from a height of 32 inches upon a corner of the plate held on a wooden block. The weight of the ball was 67 grams and this delivered a blow of 0.4 foot-pound.

III. Antimony Plating Experiments

To produce a galvanic plating of antimony upon sheet steel it is, of course, necessary to have some suitable solution of antimony salts in which the desired reactions will take place. The antimony salts most readily available for the purpose are potassium antimonyl tartrate, more commonly known as tartar emetic, and antimony trichloride.

Tartar emetic dissolves readily in water without hydrolysis, and for that reason is easy to use. Antimony trichloride hydrolyzes readily and its use requires a somewhat different technique. It may readily be dissolved in a number of non-aqueous solutions such as benzol, alcohol, and carbon tetrachloride. It may also be made up in hydrochloric acid or in concentrated common salt solutions in which case the ionization of the acid or salt represses the hydrolysis. Other forms of antimony, which may be used but are not so desirable, are antimony pentachloride, which is not very stable, and antimony trifluoride, which is highly corrosive.

IV. Tartar Emetic Solutions

Preliminary trials using a regular white cover coat as a base enamel were conducted with several solutions of tartar emetic. The solutions investigated were 5 and 20% in neutral solutions and in 10% tartaric acid solutions. The 20% solutions were used at a temperature of 160°F to keep this amount of tartar emetic in solution.

Plating in the neutral solutions developed a light-colored metallic deposit, whereas the acid solutions developed a dark blue deposit. In the weaker solutions a 5-minute bath sufficed to develop a good plate. In the stronger concentrations, 2- to 3-minute baths were ample. The enameling trials showed some fishscaling and aside from this were satisfactory. The plates were all right in finish white. The adherence was fair. Extending the time of the plating bath in the stronger solutions to 5 and 7 minutes resulted in a heavier deposit of antimony plate which led to considerable boiling in the ground-coat fire.

V. Antimony Trichloride Solutions

A number of concentrations of antimony trichloride in saturated salt (NaCl) solutions were investigated. These were 0.5, 1, 5, 10, and 20%.

The low concentrations produced a "sooty," black deposit of antimony, probably that form of metallic antimony known as antimony black. Agitation of the solutions with an electric stirrer tended to build up a heavier deposit around the edges of the plate. Two- to four-minute plating baths produced a sufficient plate in the weak

solutions. Results obtained with the 5% solution were somewhat variable, sometimes a black deposit and sometimes a bright metallic plate being obtained. With the 10 and 20% solutions, a bright metallic plate was obtained. A 2- to 4-minute dip in the 10% solution proved the most satisfactory for securing a bright type of plating.

Base enamels applied over the black type of deposit included the regular white cover enamel, Nos. 1, 7, 14, and 21 ground coats. In general a fair degree of adherence was developed. Ground coat No. 1 developed excellent adherence, closely approaching that developed by a blue ground coat. However, it had poor opacity and consequently failed to show sufficient opacity in finish. Number 7 ground coat had a fairly good opacity, was fairly smooth, had a tendency to fishscale, and had a decided tendency to specking which carried over into the finish coat. The adherence was fairly good. Ground coat No. 14 with a mill addition of 8% of zirconium oxide had a slight yellowish white cast, fair opacity, displayed occasional slight specking and slight fishscaling. It finished well and the adherence was fairly good. Ground coat No. 21 had some opacity and evidenced slight specking. In finish white there was some specking and the adherence was fairly good.

While the black type of deposit produces a good grade of adherence, certain inherent features of this plating make its use undesirable. The "sooty" deposit loosens and comes off into the ground-coat enamel during the dipping process, and continued dipping in a quantity of enamel would soon build up such a concentration of this material that it would materially affect the properties of the ground coat. Wiping off the loose "sooty" material leaves an adherent black plate, but this operation does not improve the enameling results.

Base-coat enamels applied over the bright type of plating included ground coats Nos. 7, 14, and 21. Number 7 ground coat developed a fair adherence, but showed considerable fine specking and a tendency to fishscale. Ground coat No. 14, with a mill addition of 8% of zirconium oxide, exhibited a slight tendency to fishscale and to specking which carried over into the finish coat. Ground coat No. 21 gave quite good results aside from a tendency to slight specking which carried over into the finish coat. The adherence was fairly good and the opacity in finish was satisfactory.

As the time of plating is increased from 4 to 8 or more minutes, boiling in the base coat appears and becomes worse as the deposit of antimony plate becomes heavier.

Trials of a bright plating on stock etched with 12% nitric acid, as will be detailed later, coated with No. 28 and No. 33 ground coats, showed in each case bad specking with attendant pits. The adherence was good.

The specking manifested in ground coats applied over the black antimony plate was much less prominent than the specking in ground coats applied over the bright type of plating. The prominent specking in ground coats applied over the bright plating of antimony was examined with the microscope at a magnification of 50 diameters. These specks appeared to be the result of a violent eruption or explosion apparently under the antimony plating. The eruptions were so violent that small bits of black debris, possible antimony plate, were scattered for some distance around the speck. Sometimes these minute bits of black were found as far as an inch away from the speck from which they originated. Usually, there was also a cluster of small red bubbles resembling a bit of red foam which was tossed to one side or the other of the pit of the speck, sometimes being thrown entirely out upon the surface of the enamel. One can only conjecture as to whether the possible causes of the eruptions are slight gas pockets under the plating or the low melting point (1166°F) of antimony.

In the electroplating industry, colloids are frequently added to the plating bath to produce a finer grained deposit. An addition of gum arabic to the 1% solution of antimony trichloride in saturated salt changed the type of deposit obtained to a gray metallic deposit. This type of plate developed very poor adherence.

A 10% solution of antimony trichloride in 10% hydrochloric acid was found to plate out quite rapidly, a gray deposit being developed in 15 to 45 seconds. A base coat of regular white enamel developed fair adherence, but exhibited numerous small bare spots. Number 7 ground coat exhibited its usual specking and showed fairly good adherence.

A benzol solution containing 20% of antimony trichloride was tried. As is the customary practice with a solution of this type the plates were

dipped into the solution and then scrubbed and rinsed in running water. Scrubbing is necessary, since on withdrawing the plates from the solution the benzol evaporates quickly leaving a coating of antimony trichloride which hydrolyzes on coming in contact with water and must be scrubbed off. This treatment produced a rather mottled or speckled plate of light color. Ground coat No. 14, milled with 8% of zirconium oxide, exhibited a slight tendency to speck and a number of small lifting spots were noted. "Lifts" or "lifting spots" are those small round spots which lift free from the metal without fracturing the enamel and which may vary from $^1/_{16}$ to $^1/_8$ inch in diameter and occasionally are as large as $^1/_4$ inch or more. These "lifts" are evidenced by their much lighter color than the surrounding enamel as they have separated from the metal base. If put through in finish coat they frequently fracture in the drying or firing operations.

A solution of 5% of antimony trichloride in "prestone" did not yield very good results. In 2-minute baths, no plating developed, while in 4-minute baths, the plates were sometimes streaked with black and sometimes with a light-colored metallic plate. Regular white cover enamel applied as a base coat developed numerous small bare spots and showed poor adherence.

VI. Antimony Pentachloride Solutions

Solutions of 1% and of 5% antimony pentachloride in saturated salt solution were tested for plating action. Two- to four-minute baths in these solutions developed a gray metallic deposit. Regular white cover enamel applied as a base coat was smooth but developed poor adherence.

VII. Antimony Trifluoride Solution

An 8% aqueous solution of this material was investigated. Two- to four-minute baths produced a bluish white deposit. Coating with a regular white cover enamel showed poor adherence.

VIII. Nickel Sulfate Solution

An 8-minute bath in a 9° Bé solution at a temperature of 160°F produced plates which were rather streaky, brown-stained in appearance. Ground coat No. 21, with mill additions of either 6% tin oxide or 8% zirconium oxide, was satisfactory in appearance. Only an occasional slight tendency to fishscale was noted. However, upon applying a finish coat of white cover enamel, fishscaling appeared during the drying operation and to a lesser extent during the firing operation. The adherence was fairly good.

IX. Copper Chloride Solutions

One per cent and 10% aqueous solutions of copper chloride were tried for the purpose of producing a galvanic plating of copper. A bath of thirty seconds to two minutes in the weak solution produced a good, uniform coating of copper. Enameling trials with a regular white cover enamel exhibited poor adherence, which may be due to the high expansion of copper. Plating trials in the stronger solution produced a nonuniform spongy deposit of copper over which no enameling trials were attempted.

X. Electroplating Experiments

Electroplates of zinc, copper, and iron were investigated for their adherence-promoting properties. Base enamels tried over the zinc plating included the regular white cover enamel, a regular cobalt blue ground coat, and No. 1 ground coat. Each of these enamels showed bad bubbling and blistering and poor adherence. The bubbling is probably due to the low melting point (787°F) of zinc.

The electroplate of copper was of a more adherent type than the galvanic plate previously mentioned. Coating this type of copper plate with a base coat of regular cobalt blue ground coat produced a nice smooth base enamel with the excellent adherence usually evidenced by a ground coat of this type. Number 1 ground coat appeared smooth and translucent, but developed poor adherence over this type of plating.

Trials of regular white cover enamel over an electroplate of iron failed to develop satisfactory adherence.

XI. Enameling Results on Iron Given No Treatment

For the purpose of affording some means of judging the relative adherence developed by the various plating methods and by the etching ex-

periments which follow, the following results obtained by enameling untreated iron are given.

The regular white cover enamel used as a base coat developed considerable fishscaling which was aggravated by the drying and firing operations in applying the finish coat. The adherence was poor.

Ground coat No. 1 was gray and smooth but exhibited poor adherence. It showed large fishscales and lifting of the enamel which then fractured and flaked off.

Number 21 ground coat with a mill addition of 8% of zirconium oxide had fair opacity, was smooth, had a slight tendency to fishscale, and was good in finish aside from a tendency to specking; adherence was fair.

XII. Etching Experiments

To produce chemically a surface structure on the sheet-iron base that will by its nature grip and hold a white base enamel, some attack on the iron so as to produce a roughened surface is involved. To produce such a roughening or etching of the iron, the properties of several acids in conjunction with other agents, mostly oxidizing in nature, were investigated.

(1) Hydrochloric Acid Plus Ferric Chloride An addition of 3% of ferric chloride to 10% hydrochloric acid was used for these trials. Plates pickled in this solution, cold, for a period of 12 minutes produced slight etchings of a bright, very fine-grained, crystalline type. Appearance of the etch was judged by appearance to the unaided eye and by microscopic examination at 50 diameters. Enameling trials of ground coat No. 17 applied on this etch showed slight specking and varying degrees of lifting.

Pickling in this solution at a temperature of 150°F for a period of 12 minutes produced a more pronounced etch of a type similar to that obtained with the cold solution. Enameling trials of ground coat No. 17 showed specking and varying degrees of lifting.

(2) Sulfuric Acid Plus Sodium Bichromate An addition of 5% of sodium bichromate to 10% sulfuric acid at 150°F was used. A 6-minute pickle in this solution produced a fine-grained crystalline appearing etch of a dark color. Scrubbing with a brush did not lighten the color. Trials of ground coat No. 17 over this etch evidenced specking and lifting.

(3) Sulfuric Acid Plus Sodium Nitrate Ten per cent sulfuric acid plus an addition of 5% of sodium nitrate was used, the temperature of the solution being maintained at 150°F. Six-minute pickling developed a rather smooth appearing fine-grained etch of a dark color. Number 17 ground coat exhibited specking and lifting when applied over this etch.

(4) Sulfuric Acid Plus Ferrous Sulfide A 5% addition of ferrous sulfide to 10% sulfuric acid was made. Six-minute pickling in this solution at a temperature of 150°F resulted in a slightly etched surface of a dark gray color. This etch is difficult to describe. No sharp points were noticed, the surface being rather cindery in appearance. Trials of No. 17 ground coat exhibited specking and lifting.

(5) Nitric Acid Plus Sodium Chloride An addition of 5% of sodium chloride to 12% nitric acid was made, the solution being used cold. Six-minute pickling produced a fairly deep and sharp crystalline etch. Scrubbing with a brush washed away the stain so that the etch was very bright in appearance. Number 17 ground coat developed bad lifting when applied over this etch.

(6) Nitric Acid Concentrations of 6, 9, and 12% of nitric acid were tested for etching action. Pickling in cold 12% acid for a period of 10 minutes was found to be the most effective means of producing a deep, sharp, angular type of etch, so a considerable study was made of the effects of enameling over this type of etch. The etched plates were covered with a light iron stain which persisted even after scrubbing.

Number 17 ground coat, aside from occasional fishscaling looked very good when applied over this etch. However, in finish white it showed considerable reboiling; the adherence was good.

Number 14 ground coat, both with and without a mill addition of 8% zirconium oxide, was tried. Aside from the improvement in opacity noted with the use of the zirconium oxide the results obtained were otherwise quite similar. A number of the plates had etched in streaks, and very small lifts tended to form along the smooth streaks. These lifts did not fracture. Considerable specking from reboiling was evidenced in the finish coat of white; adherence was fairly good.

Ground coat No. 28 plus a mill addition of 6% of zirconium oxide was applied to a total of 49 etched plates and, while a good portion of the plates were free from visible defects of adherence, the remainder, due to irregularities in the etching, showed occasional slight fishscales or very small lifts. While these lifts at first showed no fracture, they frequently fractured in the drying or firing of the finish coat with attendant pockmarking of the finish enamel. No reboiling was evidenced in finish white and the finish coat was quite satisfactory except for the fishscale marks.

Number 33 ground coat, with a mill addition of 6% of zirconium oxide, was applied to 67 etched plates, and it was found to be smooth, have fairly good opacity, a slight tendency toward very fine specking, and to have a decided improvement in adherence over ground coat No. 28. Of the total number of plates, 13 showed slight fishscaling. In finish white, these plates were quite satisfactory except for the varying degrees of reboiling that were manifested. Only 10 of the plates were entirely free from reboiling, 42 exhibited slight to moderate reboiling, and 15 displayed bad reboiling.

A 7- by 10-inch plate of ingot iron and a similar plate of commercial etched iron were cleaned, and the lower half of each plate was etched in 12% nitric acid after which the plates were given a regular sulfuric acid pickle. These two plates were then coated with No. 22 ground coat (ground coat No. 21 plus an additional 1% of antimony trioxide) and, in the case of the regular iron plate, the unetched portion exhibited a considerable amount of specking as is usual where addition of more than 1% of antimony trioxide is made to the enamel batch; also the unetched portion showed several fishscales. On the etched portion of the plate, however, the specking was almost entirely eliminated and there were no fishscales. In the case of the commercially etched stock, the portion of the plate having no additional etching showed practically no specking but did contain a number of fishscales. The portion of the plate given the additional etch showed no specking and no fishscale. A similar trial of a regular iron plate in ground coat No. 28 showed bad fishscaling and lifting on the unetched portion with no fishscaling on the etched portion. Trials of this same ground coat on commercial etched stock exhibited considerable lifting and fishscaling.

It has been mentioned that there was a tendency toward irregularities of etching. There was a tendency for some of the plates to etch in streaks. Other plates, when examined microscopically, showed the sharp angular grains or projections to be rather sparsely distributed or scattered over the plate. In other cases the grains were found to be closely packed with no sparse areas. This latter condition was found to be the best in promoting good adherence.

The disadvantages of etching with nitric acid are heating up of the acid with a copious evolution of nitrous oxide fumes and rapid deterioration of the acid. As with all etches, the grains of the etch are easily wiped off with a penknife blade, and consequently etched stock could not be spun or formed without destroying the etch.

XIII. White Ground-Coat Composition

To be successful, a white ground coat must adhere satisfactorily, either through the nature of the enamel itself or through special treatment of the enameling stock, and it must possess sufficient opacity to be covered in one finish coat of enamel.

Omitting the metallic oxides from a regular cobalt blue ground coat does not solve the problem. While such a ground coat as illustrated by ground coat No. 1 developed a good adherence over a black plating of antimony, it possessed no opacity whatsoever. Mill additions of tin oxide or of zirconium oxide do not suffice to bring the opacity up to that desired. While smelter additions of 4% of sodium antimonate or of 4% of antimony trioxide improve the opacity quite markedly, such additions tend to promote boiling in the ground-coat fire, probably through increase in viscosity of the ground-coat enamel. This is further indicated by ground coat No. 7 in which, by decreasing the alumina through decreasing the feldspar, and by increasing the soda, the viscosity is lowered to such an extent that 8% of sodium antimonate is successfully carried. This enamel as previously noted showed no boiling in ground coat, but did show a tendency to specking.

Thus it becomes necessary to increase the accessory opacifiers such as fluorspar, cryolite, and bone ash. Such increases are illustrated by ground coats Nos. 14, 17, and 21. The opacity of ground coat No. 21 is further aided by the antimony trioxide present. Ground coats of this

type develop a satisfactory degree of opacity when milled with 8% of zirconium oxide.

In enameling etched stock with ground coats of the No. 14 and No. 17 type, three types of enamel defects appeared: (1) there was a very pronounced tendency for these enamels to reboil in finish white; (2) the finish coat of white enamel tended to be rather rough; and (3) there was a slight tendency for some of the plates to hairline in finish white. These defects were overcome through the development of ground coat No. 28 which has increased fluidity and a somewhat higher expansion. This ground coat exhibited no reboiling or hairlining and it gave a very smooth surface in finish white.

The addition of antimony trioxide to the enamel batch was definitely shown to increase adherence materially. Additions of 0.5, 1, 2, and 4% were tried and it was found that 0.5% was hardly a sufficient amount to use. One per cent additions, however, develop fully as good adherence as larger additions. Of course, the opacity is materially helped by larger additions. As the addition of antimony trioxide is increased to amounts greater than 1%, a considerable amount of specking manifests itself in the ground-coat fire. This specking is materially reduced by the use of etched stock. That antimony trioxide definitely tends to promote reboiling in the second coat is demonstrated by ground coat No. 33 which shows considerable reboiling and which differs from ground coat No. 28 only by the addition of 1% of antimony trioxide.

Other oxide additions added to the enamel batch for the purpose of promoting adherence were bismuth trioxide and cadmium oxide. Additions of 1% and of 5% of bismuth trioxide to the raw batch of ground coat No. 1 gave a smooth, dark, brownish-gray enamel which flaked off in large pieces. Additions of 1 and 2% of cadmium oxide gave a greenish colored enamel which bubbled very much, probably due to the low melting point (610°F) of cadmium oxide.

XIV. Summary

A successful white ground-coat enamel must adhere satisfactorily, either through the nature of the enamel itself or through special treatment of the enameling stock. It must also possess sufficient opacity to be covered in one finish coat of enamel.

Various solutions of antimony salts were investigated for development of a plating of antimony on enameling stock for the purpose of promoting adherence. Solutions of antimony trichloride in saturated salt solutions were found most satisfactory. One per cent concentrations developed a black type of plating and 10% concentrations, a bright metallic plating. The black type of plating gave fairly good adherence with a minimum of specking in ground coat. The bright metallic plating gave fairly good adherence, but developed a more prominent type of specking.

A nickel dip was found to give fairly good adherence, but the enamels developed objectionable fishscaling in the drying and firing operations.

Galvanic plating of copper from a 1% solution of copper chloride and electroplates of copper promoted poor adherence except when a blue cobalt ground coat was applied.

Electroplates of zinc bubbled or blistered in the ground-coat fire.

Electroplates of iron developed poor adherence.

Etching experiments with hydrochloric acid plus ferric chloride, sulfuric acid plus sodium bichromate, sulfuric acid plus ferrous sulfide, nitric acid plus sodium chloride, and various concentrations of nitric acid demonstrated that only the nitric acid produced an etch to which white ground coats adhered satisfactorily. A 10-minute pickle in a 12% concentration of nitric acid was found to be most suitable for producing a good etch. Slight irregularities in etching tended to produce adherence defects, but if a good, closely knit, uniform etch was obtained, satisfactory adherence resulted.

While ground coat No. 1, applied over a black antimony plating, was the only combination producing an adherence approaching that of a blue cobalt ground coat when tested by impact in ground coat, it was found that a white ground coat which demonstrated fair adherence by impact test in ground coat would give fully as good adherence in a one-coat finish white as a blue cobalt ground in a two-coat finish white.

It is necessary to compound the white ground-coat enamel with considerable amounts of the accessory opacifiers in order to build up satisfactory opacity. Even then, additions of opacifiers to the mill are necessary. Fluidity of the enamel is very important and should be high in order to decrease reboiling and produce a smooth finish coat on etched stock. An addition of 1% of antimony trioxide to the raw batch of the

enamel promotes adherence, but develops reboiling.

Strong and uniform adherence in white ground-coat enamels can be promoted through special preparation of the enameling stock either through a plating operation or by deep etching the surface. The results obtained depend upon uniformity of the preparation of the base metal and the composition of the ground-coat enamels used. It is probable that further research, making use of the technology of plating, especially in the electroplating field, would lead to the development of plates which would be more satisfactory than those reported.

METAL & THERMIT CORPORATION
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CHROME CORUNDUM*

BY FRANK W. PRESTON

Chromium is introduced into glass to give it a green color. The textbooks say that chromic oxide is very hard to dissolve in glass and that, therefore, sodium dichromate or potassium dichromate should be used. In this respect the textbooks seem to be copying one another, for the dichromates give a peck of trouble.

Several years ago a bottle manufacturer making emerald-green soda bottles called the writer's attention to the difficulty. Black stones were occurring in the glass. Microscopic examination showed that the stones were hexagonal plates, having the appearance of corundum, beautifully crystallized in many instances, but stained a deep green as if containing a high percentage of chromic oxide. Dr. Insley confirmed the diagnosis, adding that alumina and chromic oxide form a series of solid solutions in the crystal state. These crystals will be referred to as crystals of chrome corundum.

A year or two ago, in making a glass blackboard at the Standard Plate Glass Company, it was necessary to use a glass matrix of very emphatic blackness to cover up the brown color of the chromite aggregate. The natural combination for intense blackness is, of course, chromium and manganese. Before long there was a complaint that there must be coarse material in the chromite, for there were "shiners" in the blackboards. The diagnosis was this time a little more difficult on account of the opacity of the matrix, but the same trouble was found—little plates of chrome corundum.

Still later H. H. Blau complained of difficulties in making a green opal. A sample of the glass showed chrome corundum again.

Inasmuch as the trouble has occurred in so many unrelated enterprises, it may be worth while to put it on record. The difficulty is readily overcome by using some other source of Cr_2O_3 than the alkali dichromates. The bottle plant is using air-floated chromite, a very finely divided

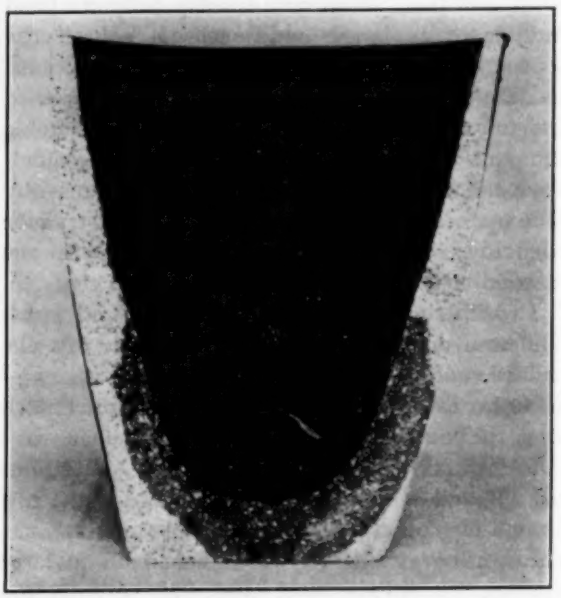

FIG. 1.—Denver fireclay crucible in which potassium dichromate was melted and heated to 2700°F. The crucible has then been cracked in two on a vertical plane. The level of the original pool of melted dichromate can be seen about 1/3 the height of the crucible from the bottom. The liquid has ascended to the top of the inside of the pot by capillarity. It has also penetrated deeply through the hard-fired clay as shown by the dark stain, and at the bottom and on one side (the right-hand side) has percolated completely through to the outside of the crucible. The interior is covered with chrome-corundum crystals.

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natural mineral. Theoretically it is ferrous chromate, or a mixture of the chromate and magnesium silicate, but it appears to be more complex than that in practice. It is very infusible and so must be finely divided, but it does not form chrome corundum.

The dichromates melt at a low temperature and when molten are very fluid and highly penetrating. They will run right through a Denver fireclay crucible. They also climb up the refractory above the flux line by capillarity. The alkali seems to combine with the silica of the refractory and the chromium reacts with the alumina to form sparkling crystals of chrome corundum. It is an interesting experiment to melt a few grams of potassium dichromate in a fireclay crucible at glassmaking heat (Fig. 1).

The Corhart Refractories Company sent the writer a Corhart block with a bowl-like cavity, as a sort of approximation to a crucible, to see how fused mullite stood up. On account of its lower porosity this material proved better than fireclay or flux blocks, but at the surface the reaction went on just the same and the same crystals formed. An improvement in refractories was therefore no complete solution. The best way is to avoid the use of the dichromates.

In practice, the concentration of dichromate is important. At low concentrations no trouble is encountered. But if there are local concentrations in contact with the refractory, there is trouble immediately. This happens automatically if the dichromate is lumpy, but it can happen to a less extent even if the dichromate is dissolved in water and spread over the sand, for it melts easily and runs away from the other ingredients.

BUTLER, PA.

AN UNDESCRIBED VARIETY OF FLINT CLAY*

BY S. L. GALPIN AND J. P. NÖLTING, JR.

ABSTRACT

The location, physical and working properties, chemical composition, and microscopic character of this flint, which has not hitherto been described, are presented.

I. Introduction

In the Conemaugh of northern West Virginia and adjoining states, there are several layers of clay rock which are rather unique in appearance and physical properties. While less hard and more porous than most flint clays, their relationship to them is closer than to any of the plastic clays. They seem to be derived in large part from volcanic ash.

The layers vary in thickness from a few inches to as much as eight feet; they also vary in purity. One bed, found near the base of the Pittsburgh red shales, seems cleaner than others.

II. Outcrop Area

Figure 1 shows the approximate outcrop area of the Conemaugh, and the circles designate localities where this type of flint clay has been found. Each occurrence is at about the same geologic horizon, coming near the base of the Pittsburgh red shale.

Natural exposures of these clays are rare. In road cuts and ditches, the crops are characterized by a yellow color, pronounced jointing, and a finely, irregularly cracked surface.

III. Physical Characteristics

Weathering produces a gravelly material made up of sharply angular particles. There is little tendency shown toward lamination, and the fracture is distinctly conchoidal. Slaking, as exhibited by most clays and shales, is wanting, although water is rapidly absorbed.

Examination of a hand specimen of the rock shows an apparently homogenous, porcelain-textured material of the color and luster of beeswax. Old fracture surfaces are brown from deposition of limonite on them. The hardness, except for impurities, is about that of the finger nail. The dry material is brittle.

Use of low magnification reveals a surprising diversity in shape and size of particles composing the clay. Some layers are of very fine texture, but others, making up usually the bulk of the rock, are considerably coarser. The presence, especially in these coarser layers, of many dark-

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appearing, translucent particles is readily seen. These particles are thin, sometimes straight, sometimes curved. Some show a complete oval or circular section. Apparently these particles are largely tubes, hollow spheres, or spheroids and fragments of the same. Scattered angular grains (quartz) are seen in the coarser portions of the rock. Irregular iron-stained areas are located along fractures and penetrate to some extent the bordering material.

IV. Mineral Constitution

Microscopic examinations of thin sections show a rock composed almost wholly of crystalline material, but of pronounced textural irregularity. The curved and oval particles mentioned are composed of finely divided crystalline material, sometimes of unit orientation, sometimes of radiate, and sometimes of heterogeneous orientation. The composing minerals of these fragments are too small for positive identification, but the low birefringence and form suggest kaolinite. Sericitic mica is also indicated in scattered minute shreds of fairly high birefringence.

V. Chemical Composition

The chemical composition[1] of a selected sample is given as follows (sample from near Morgantown, W. Va.):

	Per cent		Per cent
SiO_2	55.72	K_2O	Tr.
Al_2O_3	22.85*	Na_2O	3.08
Fe_2O_3	4.66	SO_3	0.06
CaO	0.66	Moisture	2.63
MgO	1.93	Ignition loss	8.41

* By difference.

The ratio of Na_2O to K_2O was so unusual that a check was recently made. The results confirmed the earlier analysis but show Na_2O 1.51% and K_2O 0.21%.

VI. Physical Tests

Preliminary tests of working characteristics have been run with the following results (sample from near Morgantown, W. Va.):

Material pulverized to pass a 60-mesh screen was made plastic with tap water, hand-shaped into flat bars of 1- by $2^1/_2$-inch cross-section, wire cut to test pieces approximately 1 by 1 by $2^1/_2$ inches, and dried slowly. The plasticity was rather short. Drying shrinkage (linear) averaged 8%. No cracking or warping developed; water lost on drying 18%, specific gravity 2.56.

Fired to 1050°C (cone 05), test pieces were pale red, soft, and absorbed 16% of their weight of water. Total linear shrinkage was 12.5%, specific gravity 2.54.

Fired to 1220°C (between cones 4 and 5), the color was buff, hardness above steel; absorption 8.5% by weight, total linear shrinkage 17%, and specific gravity 2.60.

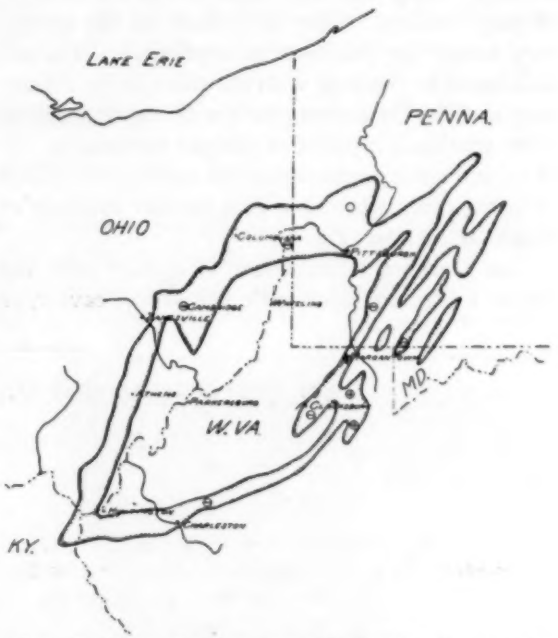

FIG. 1.—Map showing approximate location of the outcrop of Conemaugh rocks. ⊕ locality where clay bed is +3 feet thick; ⊖ locality where clay bed is −3 feet thick; ○ locality where no clay has been found.

A single test piece was carried to 1650°C (cone 29—the limit of the testing furnace) and was removed from the furnace while red hot. The quick chilling caused the piece to break into several fragments. The color was gray and the body vitreous. There was no evidence of warping. The absorption was 1% by weight and specific gravity 2.34.

The results indicate a refractory clay of No. 2 grade.

VII. Origin

The origin of this clay is uncertain. Some points of interest may be noted. No carbonaceous stains or traces have been observed. The scattered angular quartz grains, the shreds (which are considered to be volcanic in origin),

[1] Data supplied by Homer Hoskins, chemist.

and the lack of sorting of grains suggest that a considerable part of the source material was transported by wind rather than by water. The presence of minute fossils (0.25 mm.) in the clay from near Cambridge, Ohio, is puzzling but does not condemn the idea of aeolian origin. The unusual proportion of sodium to potassium (about 8 to 1) suggests accumulation in, or exposure to, highly concentrated salt water during the time that the deposit was pervious enough to be leached.

Altogether it seems probable that the source materials of the clay consisted of (1) volcanic ash, (2) products of weathering, principally quartz, clay, and limonite, and (3) shells of minute organisms. These materials were transported largely by winds and deposited in and around the margins of salt lakes, the material ultimately to become flint clay being deposited on the margins. Alteration and recrystallization, with moderate leaching, resulted in the "flinty" character of the clay.

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NOTES ON CONE 10 RAW CRYSTAL GLAZE*

By H. Thiemecke

ABSTRACT

A typical composition of a cone 10 raw glaze that possesses pronounced devitrification characteristics of commercial possibilities is given. The percentage limits of the components of the glaze, the rates of cooling and heating up, as well as the temperature range in which crystals are producible were determined. The effects of adding various types and amounts of colorants on the color and the color intensities of the crystals and the glass matrix are discussed. Optical data indicate the crystals to be members of the pyroxene group.

I. Introduction

Of the numerous investigations on crystalline glazes, results of which are recorded in the literature, none seems to have included the ideal commercial crystal glaze that (*a*) requires no fritting, (*b*) matures with the body in a single fire, (*c*) does not flow off the ware, (*d*) does not craze, and (*e*) produces crystals of pleasing habit that are consistently reproducible within limits, both as to size and number.

In the course of development of a white transparent glaze for a vitreous body of the general composition, feldspar 32%, ball clay 25%, china clay 21%, and flint 22%, within the heat treatment available in regular electrical porcelain firing to cone 10, a glaze was found which possessed a majority of the ideal crystal glaze properties listed above. This glaze had the following formula:

(A) Molecular

$$\left.\begin{matrix}0.16\ K_2O\\0.43\ MgO\\0.31\ CaO\\0.08\ ZnO\\0.02\ BaO\end{matrix}\right\} 0.24Al_2O_3 \left\{2.2SiO_2\right.$$

(B) Normative

Feldspar	35.0%	Magnesium carbonate	14.5%
Whiting	12.5	Ball clay	8.5
Zinc oxide	2.5	Flint	25.5
Barium carbonate	1.5		

Note: North Carolina feldspar and Kentucky Old Mine No. 4 ball clay were used.

The crystals in general were of uniform size and nature, spherulitic and stellate. A number were of elongated prismatic form.

II. Experimental

(A) Composition Versus Crystal Development

To determine the range of composition of the glaze in which crystals could be obtained on the tunnel kiln firing schedule shown in Fig. 1, and also if possible to bring the composition into another primary crystal field which might yield crystals of different habit and residual glass of differing characteristic, each of the components was varied separately between the following percentage limits:

* Presented at the Annual Meeting, American Ceramic Society, Cincinnati, Ohio, February, 1934 (White Wares Division). Received May 16, 1934.

	(%)		(%)
Feldspar	0–50	Magnesium carbonate	0–22
Whiting	0–18	Ball clay	0–11
Zinc oxide	0–8	Flint	0–40
Barium carbonate	0–11		

All glazes were applied by dipping at 1.60 specific gravity to the bone dry ware. The original composition showed no crystal development when the glaze was applied below 1.50 specific gravity, and above 1.65 specific gravity, without auxiliary deflocculation, the coat of glaze was so thick as to cause it to flow off the ware during firing.

The results of varying the components singly follow. Throughout the whole range of compositions, wherever crystals developed, they were all of the same phase.

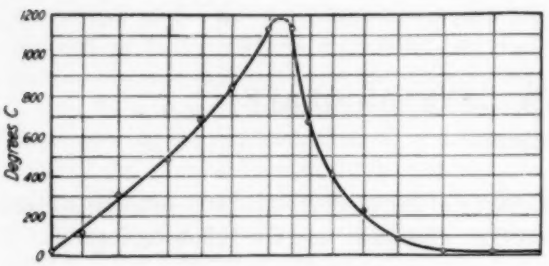

FIG. 1.—Tunnel kiln firing schedule; 6-foot car length, 59-car tunnel; schedule 3 hours.

(1) Feldspar Series From 50 to 45% feldspar there were no crystals and the glazes possessed a high gloss. From 45 to 30% good crystal development resulted, the crystals growing larger as the feldspar content approached 30% where they averaged $^1/_8$ inch in diameter. From 30 to 0% there were crystals throughout. With decreasing feldspar content, the crystals became more profuse and smaller, but the glaze as a whole became less viscous at elevated temperatures and did not cover sharp edges of the ware well. Crystallization limits were found to be 0 to 45% feldspar.

(2) Calcium Series From 0 to 7.5% whiting there were no crystals and the glazes possessed an eggshell surface due to insufficient fluxing at this temperature. From 7.5 to 14%, good crystal development resulted, the crystals becoming larger toward the high lime content. From 14 to 18% the glazes became too fusible and flowed to the bottom of the ware where crystals developed. Crystallization limits were a minimum of 7.5% whiting; maximum not determined.

(3) Zinc Series From 0 to 1.5% zinc oxide the crystals were very profuse and fine, producing almost mat glazes. From 1.5 to 3% good crystal growth resulted, the crystals averaging $^1/_8$-inch diameter. From 3 to 8% the fluxing effect was too great and the glazes tended to flow to the bottom of the ware where crystals developed. Crystallization limits were a minimum of 0.0% zinc oxide; maximum not determined.

(4) Barium Series The action of barium was similar to that of zinc but showed greater fluxing power per given percentage weight variation. With 0.0% barium the crystals were very fine and profuse, producing a finish closely approaching a mat. With a trace of barium, the crystals became larger and more sparse, toward 2.5% barium carbonate, above which the glazes flowed to the bottom of the ware and crystals developed in the thick beaded portions of the glaze. Crystallization limits were a minimum of 0.0% barium carbonate; maximum not determined.

(5) Magnesium Series At 0% magnesium the glaze was eggshelled, decreasing in eggshell toward 10% magnesium carbonate content where a good transparent glaze resulted. At 12% magnesium carbonate, crystals began to develop, growing larger and more profuse to 16% magnesite, at which the glazes became mat. Crystallization limits were a minimum of 12% magnesite, maximum not determined.

(6) Clay Series Throughout the series very regular crystal development resulted. At 0% clay the crystals were largest, averaging $^3/_{16}$ inch in size and reducing to $^1/_{16}$ inch at 11% clay content. Crystallization limits were a minimum of 0% clay; maximum not determined.

(7) Flint Series With 40% flint content, the glaze showed a profuse growth of crystals. However, the glaze was not a mat. As the flint was decreased to 20% the crystals became larger and more sparse, after which the glazes were so fusible they flowed to the bottom of the ware and crystals developed in the beaded portions to 8% flint content when crystallization stopped. Below 20% flint content the glazes crazed. Crystallization limits were a minimum of 8% flint; maximum not determined.

(B) Firing Versus Crystal Development

To ascertain the effect of rate of cooling on the crystal development of this type of glaze, composition B is given.

Feldspar	36.0%	Magnesium carbonate	15.0%
Whiting	13.5	Ball clay	5.0
Zinc oxide	2.5	Flint	26.0
Barium carbonate	2.0		

On the firing schedule of Fig. 1, this composition, which showed the best commercial possibilities, was fired at 100°C per hour rise at the maturing range of the glaze (cone 10) and then cooled at different rates ranging from 40 to 400°C per hour.

FIG. 2.—Interlocking crystals obtained on 40°C per hour cooling schedule.

This procedure was facilitated by determining the temperature range through which the crystals developed. The respective cooling schedules later were maintained only through this range. In determining the devitrification range (as a matter of convenience the temperature was arbitrarily dropped 100°C per hour) samples of the glazed ware were withdrawn from the muffle kiln at 25°C intervals and were quenched in room atmosphere.

At 1300°C, there was fine uniform crystal development, the crystals being about the size of a very small pin head and increasing in size to 1100°C. Seemingly, per given area, there was the same number of crystals developed from 1300 to 1100°C, but as the temperature of quench was lowered the crystals had more chance to grow, and whereas at 1300°C they were $^1/_{16}$ inch in size, they developed to $^1/_8$ inch at 1100°C.

The various cooling rates maintained through the devitrification range gave the following results:

(1) On the 40°C per hour schedule, the crystals were developed to such an extent that they interlocked, giving a coarse matted effect as shown in Fig. 2.

(2) On the 60°C per hour schedule, the crystals were still somewhat interlocked but at occasional spots the glass matrix showed between the crystals.

(3) On the 100°C per hour schedule, all the crystals were separated and of $^1/_8$-inch uniform size.

(4) On the 200°C per hour schedule, the crystals had reduced to $^1/_{16}$ inch in size (Fig. 3).

(5) On the 300°C per hour schedule, the crystals had just enough opportunity to begin to develop before the glass matrix became too viscous for further development and resembled pin points. At this cooling rate the glaze crazed.

FIG. 3.—Separated crystals obtained on 200°C per hour cooling schedule.

(6) On the 400°C per hour schedule, no crystals were found and the glaze crazed.

The possibility that variations in heating up might be influential presented itself and, as a check, glaze samples were brought to cone 10 in four hours and then cooled at 200°C per hour. As with the smaller increment heating schedule, there resulted the same crystal development, the only effect of fast firing being to produce occasional pinholes due to insufficient time for the glaze to flow and cover avenues of gaseous escape.

(C) Addition of Colorants

Colorants were introduced as direct additions to composition B, fired in the muffle kiln at 100°C per hour at the maturing range of the glaze, and cooled at 200°C per hour. The effects were as follows:

Colorant	Addition (%)	Color of glass matrix (Min. addition)	Color of glass matrix (Max. addition)	Color of crystals (Min. addition)	Color of crystals (Max. addition)
MnO_2	2–10	Light brown	Dark brown	Cream	Flesh
Fe_2O_3	2–10	Greenish brown	Dark brown	Fawn	Light brown
Cr_2O_3	0.5–2.5	Pale green	Apple green	Emerald green	Emerald green
$Na_2U_2O_7{\cdot}6H_2O$	2–10	Yellow-green	Yellow-green	Canary yellow	Gray (powdered zinc)
CuO	1–5	Apple green	Dark green	White	White
$CoSO_4{\cdot}7H_2O$	1–5	Powder blue	Navy blue	Pink	Pink
Black stain	2–10	Blue-black	Blue-black	Fawn	Light brown
Pink stain	2–10	Clear	Pale green	Opaque white	Opaque white

It is significant to note that only when copper was used as a colorant did the crystals remain unaffected in color. Further, it is of interest that the color of the crystals with cobalt addition was pink, possibly due to the interaction of the magnesium and cobalt oxides[1] and that the color intensities of the crystals in the case of cobalt and chromium additions as well as of the glass matrix when sodium uranate was used remained constant as the amount of colorants varied. When the stains, composed of a number of oxides, were made the colorants, the crystals seemed to show a preferential affinity for one of the components, *i.e.*, the iron oxide of the black stain and the tin oxide in the case of the pink stain. The other component of the pink stain, chromium oxide, as its concentration attained sufficient proportions to manifest itself, imparted its characteristic green color to the glass matrix.

(D) Nature of Crystals

At first the crystals, when viewed macroscopically, were thought to be willemite ($2ZnO \cdot SiO_2$), but the fact that they formed even after the zinc oxide was omitted from the glaze and when subjected to the action of hydrochloric acid did not gelatinize as does willemite[2] tended to disprove such formation. Consequently, fragments of the crystals were chipped from the glaze containing no colorant and examined under the microscope. As previously mentioned they were stellate, spherulitic, and in some cases elongated. Due to the crystals being small and partially enveloped by glass, positive identification was difficult and, as far as it could be determined, the index was close to 1.67 and the extinction angle 38°, thus throwing the crystal in the pyroxene group, probably the monoclinic form diopside ($CaOMgO \cdot 2SiO_2$). With the later introduction of the colorants to the glaze, through solution, this form probably reverted to other types; for example, chrome diopside and augite in the case of the sesquioxides of chromium and iron, respectively. The color of the crystals obtained confirm such changes.

[1] R. T. Stull and G. H. Baldwin, *Trans. Amer. Ceram. Soc.*, **14**, 764 (1912).

[2] A. N. Winchell, Elements of Optical Mineralogy, p. 163. John Wiley & Sons, Inc., New York, 1927.

Usually large crystal effects appeal more to the ceramic art trade, and although the maximum size of the crystals obtained in this investigation was $^3/_{16}$ inch, the possibility exists that larger pyroxene crystals as observed in nature might be obtained artificially with a glaze of this type. Further variations in composition and cooling treatment probably would produce the desired effect.

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CERAMIC ABSTRACTS[1]

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Vol. 13 **November, 1934** **No. 11**

Abrasives

Dressing and truing of grinding wheels. Anon. *Amer. Machinist*, **78** [19], 646 (1934).—Factors to consider in selecting proper size diamonds for dressing and truing abrasive wheels are wheel diameter, thickness of wheel face, grit, grade, bond, and abrasive. Angles at which to apply the diamond for best results in dressing up the wheels are discussed. Illustrated. E.J.V.

Properly set up polishing wheels assure economical operation. Fred B. Jacobs. *Metal Cleaning & Finishing*, **6** [8], 427–28 (1934).—To obtain economical service from polishing wheels care must be used in setting them up. The equipment necessary consists of a glue heater, a number of abrasive troughs, a preheating oven, and drying racks. The setting-up room should be near the polishing room and should be closed in to prevent chilling drafts of air from striking the wheels and glue, the temperature being at least 80°F summer and winter. Only high-grade glues should be used and only enough glue to last about 2 hr. should be prepared at a time in order to use it at its greatest strength. Detailed instructions for the setting up of the wheels are given, with necessary precautions for best results. E.J.V.

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Chinese ceramic sculpture, Kansas City. ANON. *Art*, **27** [6], 342–43 (1934).—The last of a group of eight pottery Lohans of the T'ang dynasty has been bought for the Nelson Museum. These great ceramic figures were undoubtedly modeled, fired, and glazed in the caves where they were found. Illustrated. E.B.H.

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Earthenware and china. ANON. *Amer. Home*, **11** [2], 92 (1934).—New earthenware and china designs are described and illustrated. F.G.H.

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Newton, London and New York, 1933. 173 pp. Price $3.75. Reviewed in *Mech. Eng.*, **56** [3], 187 (1934).—The applications of Ostwald's theory of color to color measurement, color mixtures, and pigments are discussed. For Part I see *Ceram. Abs.*, **11** [3], 153 (1932). F.G.H.

Machine Art. PHILIP JOHNSON. Foreword by A. H. Barr, Jr. New York Museum of Modern Art, 1934. Reviewed in *Times Lit. Supp.*, **33**, 444 (1934).—Porcelain, glass, and other industrial units are treated for the purpose of adding beauty to efficiency. H.H.S.

Plano-Convex Brick and Their Use in Ancient Oriental Civilizations. The Treatment of Clay Tablets in the Field. P. DELOUGAZ. xi + 57 pp. University of Chicago Press, Chicago, 1934. Reviewed in *Times Lit. Supp.*, **33**, 283 (1934). H.H.S.

PATENTS

Apparatus and method for the comparison of colors. H. H. SHELDON AND C. F. LORENZ (Sheldon Electric Corp.). U. S. 1,971,317, Aug. 21, 1934.

Designs for:

Bottle. G. B. LAUFER. U. S. 93,193, Aug. 28, 1934. W. R. LEACH (Carr-Lowrey Glass Co.). U. S. 93,116 and 93,117, Aug. 21, 1934. E. G. WESTLAKE (Marshall Field & Co.). U. S. 93,062 to 93,077, Aug. 14, 1934.

Gas range. A. H. MOECKER (American Stove Co.). U. S. 93,122, Aug. 21, 1934.

Glass goblet. E. H. MANN. U. S. 93,120, Aug. 21, 1934.

Glass tumbler. A. H. NICHOLSON (Federal Glass Co.). U. S. 93,177 and 93,178, Aug. 28, 1934.

Jar. C. C. NOBLE (Tygart Valley Glass Co.). U. S. 93,179, Aug. 28, 1934.

Plate. J. E. GOODWIN (Josiah Wedgwood & Sons, Inc., of America). U. S. 93,216 and 93,217, Sept. 4, 1934. ALBERT REISNER (Heinrich & Winterling, Inc.). U. S. 93,131, Aug. 21, 1934. GUSTAV STAELIN. U. S. 93,187, Aug. 28, 1934.

Range. ORRIN HOFFERBERT (Malleable Iron Range Co.). U. S. 93,221, Sept. 4, 1934. ARTHUR STOCKSTROM AND A. H. BRODBECK (American Stove Co.). U. S. 93,250 and 93,251, Sept. 4, 1934.

Stove. C. J. ROGERS (Crown Stove Works). U. S. 93,182, Aug. 28, 1934.

Device for taking multicolored photographic pictures. E. RECKMEIER. Brit. 414,257, Aug. 9, 1934.

Cements

Analysis of mixtures of hydrates of alumina and of calcium aluminates. HENRI LAFUMA. *Chim. & ind.* [Special No.], **31** [4 bis], 234–35 (1934); abstracted in *Ind. chimique*, **20** [238], 836 (1933).—The method consists in calcining the mixture to 600° for 1 hr. and treating the cold residue with a *N*/10 surplus HCl. The free alumina becomes insoluble; the combined alumina, which is soluble, is found in the acid solution with the lime. This method was used to confirm the existence of the hydrated dicalcium aluminate and the formation of this salt in the hydration of aluminous cements. M.V.K.

Celite ($4CaO \cdot Al_2O_3 \cdot Fe_2O_3$) in Portland cement. SHOICHIRO NAGAI AND GENTARO SAWAYAMA. *Jour. Soc. Chem. Ind.* [Japan], **37** [5], 264–67*B* (1934).—The results are shown in tables. M.V.K.

Cements of high quality. F. FERRARI. *Tonind.-Ztg.*, **58** [53], 635–37 (1934).—The relationships between the hydraulic factors and the strength of cement are discussed. Bibliography. M.V.K.

Chemical constitution of Portland cement clinker. II. W. WATSON AND Q. L. CRADDOCK. *Cement & Cement Manuf.*, **7** [2], 54–58 (1934).—After a discussion of early theories of solid solution and hypothetical structural formulas, the application of the phase rule to Portland cement research is treated. **III.** *Ibid.*, **7** [4], 111–17 (1934).—A discussion is given of the researches of Rankin and Wright on the system CaO–Al_2O_3–SiO_2. Although this system is most important, a complete understanding of the constitution and behavior of Portland cement can not be available until the compounds developed in other systems, including such compounds as Fe_2O_3 and MgO, have been worked out. G.R.S.

Determination of the commercial value of mortars mortar mixtures, and cement mixtures. FRANCESCO OCCHIPINTI. *Atti IV congr. naz. chim. pura appl.*, pp. 759–72 (1933).—Mechanical examination of hardened, stored mixtures showed that drawing conclusions as to the original proportions of very complicated mixtures is impossible, but that the inclusion of organic substances, clay, and nonhomogeneous mixtures can be shown. The literature is reviewed. (*C.A.*)

Formation of oxychlorides rich in chlorine. P. MECKE. *Tonind.-Ztg.*, **58** [57], 689–90; [58], 700–701; [59], 713–15 (1934).—Attempts to determine quantitatively the chlorides combined with cement, calcium aluminates, and lime are described. M.V.K.

Heat of hydration of cement and its constituents. II. O. F. HONUS. *Cement & Cement Manuf.*, **7** [7], 208–10 (1934).—The heats of hydration were calculated as follows:

Compound	Heat of Hydration (K cal./mol.)	(cal./g.)
$CaSiO_3$	− 0.5	− 4
β-Ca_2SiO_4	+ 5.7	+ 33
γ-Ca_2SiO_4	− 2.1	− 1.2
Ca_3SiO_5	+20.3	+ 89
$Ca_3Al_2O_6$	+54.8	+203
$Ca_2Fe_2O_5$	+ 2.0	+ 7
Mg_2SiO_4	− 1.0	− 7
CaO	+14.9	+ 2.26

III. *Ibid.*, **7** [8], 244–53 (1934).—An increase in the tricalcium silicate content of a cement is not necessarily accompanied by a rise in strength; this depends upon (1) fineness of grinding and (2) extent of hydration. The curves for strength and total heat of hydration are nearly parallel, and both are strongly influenced by variations in the tricalcium aluminate and dicalcium silicate contents.

A small sieve residue is not always associated with high strength, especially when a cement has a very low tricalcium silicate content. It is shown that the tricalcium silicate content of a cement can influence its strength to a great extent, regardless of the grain size or whether or not the hydration is complete. In these cases the heat of hydration curve is nearly parallel to the strength curve. The particle size of the principal hydraulic compounds governs the development of strength. Attention must be paid to the presence of free lime in determining the rational composition of cement. For Part I see *Ceram. Abs.*, **13** [9], 231 (1934). G.R.S.

Heat of solution method in the calorimetry of Portland cement. R. W. STENZEL AND S. B. MORRIS. *Ind. Eng. Chem., Anal. Ed.*, **6** [4], 246–49 (1934).—The authors indicate the precautions necessary to attain a reasonable accuracy. The method given is especially designed for measuring the heat of hydration of cement at various ages. Zinc oxide is suggested as a suitable secondary standard for heat-capacity determinations. Illustrated. F.G.H.

Hydration of Portland cement compounds. R. H. BOGUE AND W. LERCH. *Ind. Eng. Chem.*, **26** [8], 837–47 (1934).—A general theory has been developed which permits an understanding of the chemical and physical mechanism of the hardening process. The effects of the aluminates on the silicates are indicated both in the absence and presence of a retarder. Illustrated. F.G.H.

International dictionary of cement. C. R. PLATZMANN. *Cement & Cement Manuf.*, **7** [5], 153–56 (1934).—Terms are given from C to H in Spanish, French, English, and German. *Ibid.*, **7** [8], 260–62 (1934).—Terms from R to Z are included. For H to R see *Ceram. Abs.*, **13** [9], 231 (1934). G.R.S.

Italian cement specifications. ANON. Abstracted in *Cement & Cement Manuf.*, **7** [5], 119–22 (1934). G.R.S.

Italian pozzuolana and pozzuolanic Portland cement. S. NAGAI AND I. YOSHIDA. *Cement & Cement Manuf.*, **7** [8], 254–57 (1934).—Chemical analyses and results of compression tests are shown in tables. G.R.S.

Plaster molds for producing tile. J. WELTER. *Rev. mat. constr. trav. pub.*, No. 298, pp. 121–23*B* (1934). M.V.K.

Researches on the hydration of Portland cement. XIII–XVI. KATSUZO KOYANAGI. *Jour. Soc. Chem. Ind.* [Japan], **37** [3], 113–17*B*; [5], 243–49*B* (1934).—Tricalcium aluminate is hydrated to $3CaO \cdot Al_2O_3 \cdot 10H_2O$. For Parts XI–XII see *Ceram. Abs.*, **13** [7], 170 (1934). M.V.K.

Swiss specification for cements. ANON. *Cement & Cement Manuf.*, **7** [7], 229–30 (1934).—A summary is given for new specifications. G.R.S.

BOOK REVIEW

Increase of Mechanical Strength of Gypsum Molds for Porcelain and Faience Manufacture. I. P. ROMANKEVICH AND R. B. ANGENITSKAYA. Ukrainian Sci. Research Inst. Bldg. Materials of Mineral Origin. Ukrainian State Pub. House of Light Ind., Kharkov, 1933. 28 pp. Price 1 R. S.I.PERKAL

Enamels

Acid-stable enamels. L. VIELHABER. *Emaillerie*, **1** [9], 11–13 (1933); abstracted in *Emailwaren-Ind.*, **11** [31], 262 (1934).—V. discusses general viewpoints on the composition and working conditions of enamel resistant to acids. The SiO_2 content must amount to at least 50, B_2O_3 at least 20, Al_2O_3 3, Na_2O 18, ZnO 7, CaF_2 at the most 1, and antimony oxide, as opacifier, 5%. Several compositions are given. See also *Ceram. Abs.*, **13** [2], 32 (1934). M.V.K.

Adherence of ground enamel containing cobalt and nickel oxides. FRIEDRICH HEIMES. *Sprechsaal*, **67** [16], 231–32 (1934).—The researches of Dietzel and Meures (*Ceram. Abs.*, **13** [2], 31 (1934)) and Schaarschuh (*ibid.*, **13** [6], 142 (1934)) on the adherence of ground enamel on sheet iron are discussed in detail. A series of electrolytes with enamels containing copper, nickel, and cobalt oxides was made to determine the electrolytic behavior of the enamels. It was found that between the sheet iron, enobled by the deposition of nickel, the melting enamel, and the ordinary sheet-iron electrolysis produces a further deposition of nickel on the iron, and that the enamel solidly adheres on the cathode but not on the anode. M.V.K.

Adherence problem for sheet-iron enamels. A. DIETZEL. *Sprechsaal*, **67** [18], 265 (1934).—Comments on the papers of Heimes (see preceding abstract) on the adherence of ground enamels containing cobalt and nickel oxides and of Schaarschuh on the adherence of sheet ground enamel (*Ceram. Abs.*, **13** [6], 142 (1934)) and a brief review of experiments made by D. on the adherence of sheet-iron enamels are given. See also *ibid.*, **13** [10], 250 (1934). M.V.K.

Advantages of an up-to-date enameling kiln. A. JAESCHKE. *Glashütte*, **64** [22], 367–71; [24], 404–405 (1934).—The operation of semigas, generator gas, tunnel, and electric kilns for enameling is discussed in detail. M.V.K.

Annealing quenched steel. H. ESSER AND H. CORNELIUS. *Arch. Eisenhüttenwesen*, **7**, 693–97 (1934).—Nonalloyed and carbon steels were quenched after the formation of austenite. Three reactions were found on reheating the samples. The reactions increase with an increasing carbon content of the steel. The first reaction occurs between 100 and 150°C, being explained by the return of ferrite into the cubic lattice. (The assumption is made that martensite will form a mixture of tetragonal ferrite and cementite.) The second reaction shows a maximum at 280°C, caused by the decomposition of the remaining austenite into α-iron and iron carbide. The third reaction follows immediately after the second one, being explained by the formation of a cementite lattice. The second and third reactions may overlap in steels

high in carbon. Under-eutectic steels, quenched between 1050 and 1150°, show a fourth thermal reaction between 330 and 350° caused by a rearrangement within the γ-mixed crystals around 1000°. The remaining austenite shows a maximum for a sample quenched with just the critical velocity in order to prevent the formation of troosite. Higher and lower rates of quenching result in a smaller amount of austenite at room temperature. W.M.C.

Cadmium red enamels. L. STUCKERT. *Glashütte*, **64** [22], 364–65 (1934).—Cadmium red or fire red is a mixed crystal of cadmium sulfide and selenite formed in the temperature interval of 470 to 650°. Cadmium red is a pigment added to the mill. It is destroyed when melted with the enamel batch. Under the effect of saltpeter it is oxidized into the colorless selenite stage. The reaction between fluorine and selenium with the formation of selenium fluoride destroys the pigment, hence fire red is fritted at 600° with the melted and finely ground enamel. Up to 20% (of the weight of the batch) of the pigment is added. From 2 to 4% (weight of the enamel frit) of cadmium red is added to the mill. The color tone depends on the selenium content (15% Se yields orange red, 17% Se high red, 19% Se dark red). Additions of opacifiers (tin oxide, zircon dioxide) make the color lighter. Additions of clay to the pigment or opacifiers containing antimony are not recommended. The presence of zinc oxide in the batch darkens the color tone; lead oxide produces a deep dark red and a fiery luster in the enamel, but if too much of it is present the enamel becomes too dark. Quartz and feldspar have little effect. A high soda content improves the red tone. Generally, every good white enamel not too strongly opacified and not too hard is suitable for cadmium red. A series of cadmium red enamels is given. See also *Ceram. Abs.*, **13** [8], 198 (1934). M.V.K.

Causes and prevention of chipping of enameled cooking ware. RICHARD ALDINGER. Translated in *Ceram. Ind.*, **23** [3], 134–37 (1934). E.J.V.

Chemical elements interesting to the enamel industry. VIELHABER. *Emailwaren-Ind.*, **11** [30], 252–53 (1934).—(1) Alkali metals: compounds of potassium and lithium are usable materials; the effect of rubidium and caesium is not yet known. (2) Alkaline earth: compounds of calcium and barium are used; strontium acts as a flux and is used sometimes. (3) Magnesium group: magnesium is used as carbonate or oxide; the effect of beryllium oxide is not clear. (4) Aluminium is used as alumina and is introduced by clay, kaolin, or feldspar; cerium is added as opacifier. (5) Zinc oxide is used as a flux, increasing the luster of the enamel; cadmium is only used as cadmium sulfide and with selenium. Cadmium compounds are unhealthy and should not be used in enamelware for cooking, drinking, etc. (6) Iron group: iron, nickel, cobalt, and manganese are all used as colorizers; nickel and cobalt oxides are also used as adhering oxides. (7) The chrome-molybdenum group is less interesting; chrome and uranium are pigments, while molybdenum and tungsten are not used. (8) Lead-tin group: lead or minium is an enamel raw material; lead oxide dissolves other metal oxides and is an excellent flux; tin oxide is the chief opacifier. (9) Copper group: copper is used as a pigment; silver is mentioned in a patent for the production of enamel as silver metal; it should have the effect of an adhering metal such as Co or Ni. The precious metals, gold and platinum, are used only for decorations. The other metals of this group are uninteresting. (10) Nonmetal elements and metalloids: fluorine is most important, phosphorus as bone ash is an old opacifier, arsenic is used only in powder enamel for shields, antimony (tri- and pent-oxide) is a known opacifier, bismuth is not yet used, boron as borax is the usual flux, silicon or silica is the basic material of enamel, and titanium oxide and zirconium are opacifiers. Germanium and thorium have no importance for the enamel industry. M.V.K.

Compositions of enamel batches. L. VIELHABER. *Emailwaren-Ind.*, **11** [15], 130–32; [20], 171–74; [21], 178–79; [22], 186–89; [26], 220–22; [27], 227–28; [28], 235–37 (1934).—These are excerpts from a book by L. Vielhaber, Production of Enamel Batches, at present out of print. A detailed discussion is given of (1) the effect of some raw materials on the enamel, (2) coat enamels, (3) white enamel for cast iron, (4) glazes, (5) powder enamel for shields, (6) lead enamel, (7) powder enamel for bathtubs, (8) majolica enamel, (9) acid-stable enamels, and (10) enamel for copper and brass. Various data on enamels, such as enamel constants, hardness scale of Mohs, etc., are given. See also *Ceram. Abs.*, **13** [8], 200 (1934). M.V.K.

Delay in enameling pickled sheet iron. E. G. PORST AND H. G. WOLFRAM. *Jour. Amer. Ceram. Soc.*, **17** [10], 297–300 (1934).

Desulfurizing with fused soda ash. G. E. EVANS. *Foundry*, **62** [5], 26–62 (1934).—The foundry practice of desulfurizing metal through the use of fused soda ash is described in detail. F.G.H.

Determination of fineness of grinding of enamel by sedimentation method. W. DAWIHL. *Keram. Rund.*, **42**, 109–10 (1934); abstracted in *Emailwaren-Ind.*, **11** [15], 134 (1934).—The control of the fineness of grinding of a coat enamel by means of the Pemco-Sieve is not always satisfactory. The sieve residue of two enamels was almost identical, while marked differences were observed in practical behavior. When using the standard sieve No. 100 (10,000 mesh/sq.cm.), differences in the fineness were recognized. The determination of total grain structure with the aid of the Andreasen apparatus gave good results. M.V.K.

Determination of sulfur. H. J. KARMAUS. *Emailwaren-Ind.*, **11** [23], 194–95 (1934).—The commonly used method of Schulte for determining sulfur in cast iron is based on the fact that when iron is dissolved in concentrated hydrochloric acid, the sulfur is converted into hydrogen sulfide which is conveyed into a cadmium acetate solution (which is not changed by hydrogen phosphide or arsenic hydride) and is combined as cadmium sulfide. The determination is concluded gravimetrically or volumetrically. The method of Järvinen consists in dissolving the sample in bromium water; the sulfur is precipitated as barium sulfate which is treated with a soda extract. Details are given. M.V.K.

Educational exhibits at Fair stress durability of porcelain enamel. ANON. *Better Enameling*, **5** [8], 19 (1934).—

An exhibit in which steel balls are fired at a porcelain enamel sign at the rate of 3600/hr. and another in which porcelain enamel is exposed to the action of alkalis, acid, and hot soap solution stress the durable qualities of porcelain enamel. Illustrated. E.J.V.

Effect of structure on elasticity and tensile strength of iron. H. SCHLECHTWEG. *Arch. Eisenhüttenwesen*, **6**, 507–10 (1933).—Samples varying in the amounts of graphite and ferrite present have been tested. The influence of these variations was determined on the modulus of elasticity, E, and on the "characteristic coefficient of the material," $(B + C \cdot \sqrt[3]{\ })$. Cast-iron and brittle substances may be characterized by E and the characteristic coefficient. E depends mainly on the graphite present; it decreases with an increasing graphite content or with larger lamellae of graphite. The characteristic coefficient increases with an increasing ferrite content, small ferrite inclusions being the most efficient. The tensile strength depends mainly on the characteristic coefficient. The tensile strength is determined, therefore, by the amount of small ferrite crystals present and not by the presence of large graphite lamellae. Further experiments are proposed to study the influence of various structures on the elasticity and strength of cast iron. W.M.C.

Electrolytic reactions in glass enamel and their relation to the adherence of enamel to iron. L. VIELHABER. *Emailwaren-Ind.*, **11** [24], 201–203 (1934).—V. discusses the researches of H. F. Staley (*Ceram. Abs.*, **13** [7], 172 (1934)) on electrolytic reactions in enamel and their effect on the adherence to iron. M.V.K.

Emblem Oil adopts porcelain enamel stations. ANON. *Enamelist*, **11** [11], 20 (1934).—The new Emblem Oil Co. station at Fredonia, N. Y., is described. Illustrated. E.J.V.

Enameled ship bottoms. VIELHABER. *Emailwaren-Ind.*, **11** [26], 218–19 (1934).—An old German patent (D.R.P. 468 (1877)) suggesting the enameling of ship bottoms is discussed. M.V.K.

Enameling complicated sheet-iron parts. RICHARD ALDINGER. *Glashütte*, **64** [22], 365–67 (1934).—The chief points to be observed when enameling large sheet-iron pieces of complicated shape are (1) the use of sheet iron of high quality, uniform structure, and sufficient thickness, (2) use of simple shapes without sharp corners and edges, (3) use of an enamel of a suitable composition with the lowest possible melting point, (4) careful treatment during enameling with the use of special contrivances, and (5) careful mounting of the separate parts. M.V.K.

Fluorides in white sheet-iron enamels. A. I. ANDREWS AND E. E. HOWE. *Jour. Amer. Ceram. Soc.*, **17** [10], 288–91 (1934).

Fly specks. L. VIELHABER. *Emailwaren-Ind.*, **11** [29], 242–43 (1934).—The enameled surface sometimes shows rough elevations or depressions of various sizes. These defects are usually black or light yellow and lustrous. When treating these places with hydrochloric acid, they become yellow and the hydrochloric acid solution contains iron. The enamel is oversaturated with iron oxide in these spots. The real reason for their appearance has not yet been determined exactly. Various observations from practice are described. It seems that these specks are caused by the kiln; the muffle is never entirely tight and if there is a large amount of combustion gases these penetrate into the muffle. M.V.K.

Gases in metals, with a special consideration of noniron metals. W. KOCH. *Z. tech. Physik*, **15** [7], 280–84 (1934).—The most important method for determining gases in metals is de-gasing the molten sample in the vacuum. Gases developed are measured and analyzed. Aluminum was found to contain from 1 to 2 cm.³ of gas in each 100 g. of metal. The gas content of electrolytic zinc is proportional to the square root of the density of current during the electrolysis. The amount of gas taken up by metals under pressure follows the equation $C = K \cdot \sqrt{p}$, C being the concentration of hydrogen, K, a constant, and p, the hydrogen pressure. Data are presented of the solubility of H_2 and N_2 in aluminum, copper, and their alloys, and of the solubility of H_2, N_2, CO, and CO_2 in copper and copper alloys. W.M.C.

Graphical computation of opacity of porcelain enamels. G. H. MCINTYRE. *Jour. Amer. Ceram. Soc.*, **17** [10], 300–306 (1934).

Heat conductivity of cast iron. E. SOEHNCHEN. *Giesserei*, **21** [29–30], 311 (1934).—An ice calorimeter was developed to determine heat conductivity by comparing the cast iron to a rod of electrolytic Ni. It was found that a mixture of ferrite and elementary C has a higher heat conductivity than a mixture of ferrite and cementite. The improvement obtainable by annealing depends on chemical composition and increases with increasing C content. Contrary to electric conductivity, heat conductivity decreases with fineness of graphite. In general, all elements added intentionally or unintentionally to cast iron reduce heat conductivity, especially P and Cr, contrary to what is often stated in literature; addition of Ni with simultaneous reduction of Si increases heat conductivity. M.H.

Influence of distribution of strain and composition of the sample on the lower limit of plastic flow. E. SIEBEL AND F. H. VIEREGGE. *Arch. Eisenhüttenwesen*, **7**, 679–82 (1934).—A nonuniform distribution of strain will increase the upper limit of plastic flow if local strain is higher than the average strain. The increase was found to be higher for soft ingot steel than for hard ordinary steel. No definite rules could be established for the lower limit of plastic flow. No general formula for the upper limit being available, the load in construction work should be kept low enough to remain well below the beginning of plastic flow. W.M.C.

Less opacifier when enameling. ANON. *Giesserei Praxis*, **54**, 469 (1933); abstracted in *Emailwaren-Ind.*, **11** [27], 231 (1934).—A tunnel kiln of "Techno-Chemistry A.-G." is described. It consists of a main firing zone and a cooling zone and a second firing and cooling zone. Through this second firing, opacification with tin oxide is improved so that much less opacifier is used. The enamel layer is improved and is free from stresses. M.V.K.

Lithium oxide in enamel. VIELHABER. *Emailwaren-Ind.*, **11** [30], 250 (1934).—The use of lithium oxide and lepidolite in the manufacture of enamel is discussed. Lithium oxide has no opacifying effect and can not be used as an adhering oxide; it acts as a flux. Light ground

enamels can be produced. The best results were obtained with a batch containing 55 borax, 37 feldspar, 31 quartz, 2.5 Na-saltpeter, 11 soda, 5 calcite, 5 fluorspar, and 12.5% lithium carbonate with 10% clay and 8% quartz to the mill. M.V.K.

Magnetic investigation of the amount of austenite retained in quenched steel. M. MIKAMI. *Sci. Repts. Tôhoku Imp. Univ.*, **23** [2], 213–41 (1934).—The amount of austenite retained in quenched steel has been determined by a magnetic method. Five Swedish steels containing from 0.37 to 1.27% of carbon show that the increase of magnetization below a temperature of 150°C is due to the transformation $\alpha-\beta$ martensite, whereas that at higher temperatures is mainly due to the decomposition of austenite. The amount of austenite retained will depend on temperature of quenching, concentration of carbon in γ-iron, and the phases present before quenching. W.M.C.

Management methods for enamel plant cost control. IV. Production. ROY E. DYBVIG. *Better Enameling*, **5** [8], 14–18 (1934).—Production control comprises planning, routing, scheduling, and dispatching, so organized that the movement of material, performance of machines, and operations of labor are controlled and coördinated as to quantity, quality, time, and place. D. outlines necessary preliminary information and the functions of the production department. Material control schedule is the first step. Load charts on all machines are necessary and production must be flexible enough to make adjustments for schedule failures and changes. After the order is in progress the production follow-up and control are also important. Various plans for this are discussed. For Part III see *Ceram. Abs.*, **13** [10], 251 (1934). E.J.V.

Manufacture of enameled shields. RENIER. *Glashütte*, **64** [16], 260–61; [17], 272–73 (1934).—A brief review is given of various stages of an efficient production of enameled shields. M.V.K.

Mechanism of plastic deformation of iron single crystals. N. AKULOV AND S. RAEWSKY. *Ann. Physik*, **20** [2], 113–17 (1934).—A single crystal of iron was compressed in the direction (100). The patterns on the plane (010), which formed after passing through the elastic limit, were studied. The patterns discovered by Bitter were found to change periodically, this being explained by the gliding along the planes (100), (010), and (001) changing periodically. W.M.C.

Metal iron in enamel. VIELHABER. *Emailwaren-Ind.*, **11** [30], 251–52 (1934).—The black spots often observed in enamel are all due to particles of iron dust. The enamel, when fired, stirred, or drying, comes in contact with iron particles; waste enamel also contains iron particles. Measures taken in the U. S. to prevent the contact between the enamel and iron dust are briefly described. M.V.K.

Method of fineness test. GEORGE FOEHSE. *Enamelist*, **11** [11], 11 (1934).—A settling test used at the National Enameling & Stamping Co. (Granite City, Ill.) plant for control of the grain size of the frit particles in enamel slip is described in detail. Illustrated. E.J.V.

Methods for determining the fusibility of silicates, especially enamel. ANON. *Glashütte*, **64** [13], 220–22 (1934).—The melting point of enamels must be referred to as the softening point which depends not only on the chemical composition but especially on the ratio of fluxes to refractory materials and the viscosity of the silicate melt. Methods for determining the softening temperature, including the mathematical, optical method of Kinzie and Seger cones, are briefly discussed. M.V.K.

Methods and devices in enameling technique. MARKHOFF. *Sprechsaal*, **67** [26], 387–88 (1934).—A brief review is given of new patents dealing with various stages of enameling and firing kilns. M.V.K.

Notes on enameling. XI–XII. A.H. *Verre & Silicates Ind.*, **5** [9], 168–69; [13], 244–45 (1934).—Details of cleansing by sandblasting the ware to be enameled and a discussion of the properties of water used when grinding enamel are discussed. For Part X see *Ceram. Abs.*, **13** [6], 143 (1934). M.V.K.

Porcelain enamel on copper. VIELHABER. *Emailwaren-Ind.*, **11** [25], 212–13 (1934).—V. discusses the researches of Simpson, Sullivan, and Bole (*Ceram. Abs.*, **13** [8], 201 (1934)) on enameling copper. M.V.K.

Porcelain enamel house receives multitude of World's Fair visitors. ANON. *Enamelist*, **11** [11], 12–13 (1934).—Illustrated. E.J.V.

Porcelain enamel scores again. DOHERTY RESEARCH CO. *Better Enameling*, **5** [8], 24 (1934).—The Doreco heating element, said to consist essentially of a material of high heat conductivity (approximately that of steel) and high electrical resistivity on the order of porcelain, has a nickel chromium resistor embedded in it. The element is formed at a pressure of 4000 lb./sq. in., is fired at a high temperature, and then covered with porcelain enamel. Advantages of this element are enumerated. With the porcelain-enamel coating on the resistor no hearth plate or ceramic baffle is necessary on the furnace bottom. E.J.V.

Porcelain enamel store front. ARCHITECTURAL PORCELAIN CO. *Enamelist*, **11** [11], 19 (1934); *Ceram. Ind.*, **23** [3], 133 (1934).—Illustrated. E.J.V.

Problem of waste. ANON. *Amer. Enameler*, **7** [5], 4 (1934).—The corrosive properties of the atmosphere and their reaction on the general exterior finishing materials are described. The solution by use of porcelain enameled steel is suggested. H.T.

Progress in the field of acid-stable enamels. L. VIELHABER. *Emailwaren-Ind.*, **11** [15], 129–30 (1934).—Comments on the paper of D. B. Walters (*Ceram. Abs.*, **13** [6], 142 (1934)) dealing with attempts to increase the acid-stability of ordinary enamels are presented. M.V.K.

Properties of clay for enamel. ANON. *Glashütte*, **64** [18], 290–91 (1934).—A good enamel clay must possess a high suspending action. It should be tested for swelling capability, and the amount of water-soluble salts, alkalis, and quartz must be determined. M.V.K.

Purpose of recuperators in enamel kilns. A. JAESCHKE. *Emailwaren-Ind.*, **11** [26], 219–20 (1934).—The work of recuperators and advantages of using them are dealt with. M.V.K.

Question of fishscales. L. VIELHABER. *Emailwaren-Ind.*, **11** [18], 154–55 (1934).—Experiments with various enamels in all of which fishscales appeared are discussed.

When another kind of sheet iron was employed, the fish-scales disappeared. V. concludes that the formation of fishscales is caused by unsatisfactory sheet iron in which hydrogen, formed during pickling, penetrates into the iron and during enameling promotes the formation of fish-scales. See also *Ceram. Abs.*, **13** [4], 81 (1934). M.V.K.

Raw materials in the enamel industry. VIELHABER. *Emailwaren-Ind.*, **11** [28], 233–35 (1934).—The chief minerals and raw materials used for the manufacture of enamel, such as quartz, borax, feldspar, soda, etc., and most of the coloring oxides have been known and used for one hundred years. The same is true with most of the fluxes. The effect of some of them is briefly discussed. M.V.K.

Sheet-iron, cast-iron, and majolica enamels. M. W. GULACH. *Glashütte*, **64** [22], 355–57 (1934).—G. discusses results of the latest researches dealing with the adherence and properties of sheet-iron, cast-iron, and majolica enamels and the problems confronting the enamel industry with regard to improving the quality of the enamels. M.V.K.

Store front in New York. PORCELAIN METALS, INC. *Enamelist*, **11** [11], 19–20 (1934).—Illustrated. E.J.V.

Storing time of enamel slip. ANON. *Glashütte*, **64** [10], 172–73; [11], 184–85 (1934).—Factors conditioning the storing of enamel slip after grinding were investigated. The grinding time of enamel depends on the composition (specific gravity and grit solubility) of the frit and the clay addition which depends on the composition of the enamel and the grinding time. The storing time of the enamel slip may be shortened and the defects produced by grinding and storing may be avoided by determining experimentally the best conditions for every type of enamel. Illustrated. M.V.K.

Substitute for enamel? LG. *Glashütte*, **64** [18], 289–90 (1934).—Advantages of enameled cooking utensils over those made of aluminum, metal plated, and lacquered are briefly discussed. M.V.K.

Technical and scientific progress of the enamel industry. KARL MEURES. *Glashütte*, **64** [22], 357–64 (1934).—Pickling is done mechanically, partly electrolytically and partly with alkalis; quartz or steel grits are used for cleaning cast iron. Basalt, pumice stone, lepidolite, and phonolite are used successfully in enamel batches. Among the new suspending agents, Ultra-Sil transparent (an aluminous silicate), Electrolyte US, and Clay-oxide Alugel are used. The fluxes used instead of borax are calcium borate, mineral boron, and borolite. Minium is being replaced by plumbous silicate and baryta; barium carbonate and zinc oxide are extensively used for leadless enamels. Among opacifiers, tin oxide, antimony, zircon, and titanium preparations and gas opacifiers have not been replaced. The firing of enamel in roasting furnaces heated by gas or fuel-oil proved its merit. The technique of application has remained almost unchanged. Heat-stable alloys, especially nickel-chrome steels, are used as metallic parts of kilns and other equipment. Large plants use tunnel kilns successfully, but in the smaller plants the muffle kiln is used. Traveling grates for firing enameled cast-iron ware have been successful. Silicon carbide is chiefly used for muffle kilns. The basic problems of enameling, such as adherence, opacification, and expansion of enamels have been extensively studied. It was found that the true reason of adherence lies in the formation of an intermediate layer (composed chiefly of magnetite crystals) between the enamel and the sheet iron. The action of adhering oxides is as follows: (1) the adhering oxide is reduced into metal by metallic iron; (2) strong local currents are formed which produce a strong corrosion of the iron surface; (3) the enamel deposits in the cavities and adheres. The expansion behavior of enamel is also discussed. M.V.K.

Thermal efficiency in the enamel industry. JAESCHKE. *Emailwaren-Ind.*, **11** [31], 257–58 (1934).—The necessity of careful supervising and exact temperature measurements are dealt with. M.V.K.

Titanium oxide in enamel. L. VIELHABER. *Emailwaren-Ind.*, **11** [25], 210–11 (1934); abstracted in *Verre & Silicates Ind.*, **5** [14], 269 (1934).—For a long time attempts have been made to replace tin oxide by TiO_2 as an opacifier for enamel. TiO_2 produces a yellowish tint, however, even in the absence of fluorine compounds in the enamel. Titanium considerably intensifies the coloring due to iron. This property, however, does not exclude its use in colored and ground enamels for sheet iron or cast enamels. U. S. patent No. 1,949,479 (*Ceram. Abs.*, **13** [5], 112 (1934)) suggesting the use of titanium oxide in the production of acid-resistant enamels is analyzed in detail. M.V.K.

Up-to-date drying installation for enamel. H. KUBE. *Emailwaren-Ind.*, **11** [20], 169–71 (1934).—Conditions insuring a satisfactory drying of the applied enamel are discussed in detail. M.V.K.

Water hardness in vitreous enamel suspensions. A. I. ANDREWS AND E. G. PORST. *Jour. Amer. Ceram. Soc.*, **17** [10], 292–97 (1934).

Zirconium oxide in glasses, glazes, and enamels. C. J. KINZIE AND C. H. COMMONS. *Jour. Amer. Ceram. Soc.*, **17** [10], 283–87 (1934).

PATENTS

Fuel-control means for ranges. W. C. LINDEMANN AND A. T. SCHMIDT (A. J. Lindemann & Hoverson Co.). U. S. 1,972,627, Sept. 4, 1934.

Range. W. C. LINDEMANN AND G. C. LORENZ (A. J. Lindemann & Hoverson Co.). U. S. 1,972,628, Sept. 4, 1934.

Glass

Aluminous silicates in glass manufacture. FRIEDRICH VOGEL. *Glashütte*, **64** [17], 271–72 (1934).—An analysis of leucite (a potassium aluminous silicate of the composition $KAlSiO_2O_6$) and nepheline (a sodium aluminous silicate of the formula $(Na,K)_3Al_3Si_3O_{34}$) is given, and the experiments of Russians with nepheline in the manufacture of glass are briefly reviewed. The obtaining of pure alumina and silica from these minerals is discussed. M.V.K.

Apparatus for measuring the level of glass in tank furnaces. L. N. SHEKHIROV. *Keram. i Steklo*, **10** [6], 29 (1934).—A simple automatic apparatus for measuring the

glass level is described. The raising or lowering of the glass level is controlled by colored electric bulbs. Illustrated. M.V.K.

Architectonical element in stained glass. I. JACQUES WOLF. *Verre & Silicates Ind.*, **5** [9], 171–73 (1934).—The relationship existing between the architectural style of a building and the artistic stained glass used in it is briefly discussed. Examples from ancient history and the Middle Ages are given. M.V.K.

Architecture and new materials: glass. E. FORMICHELLA. *Case d'Oggi* [Milan], **3**, 102 (1933); abstracted in *Bibliografia Italiana* [Series C], **6** [7–8], 59 (1933).—F. discusses the development of the use of glass in construction of buildings. H.F.V.

Barium carbonate in glassmelting. ANON. *Verre & Silicates Ind.*, **5** [11], 205–208; [12], 225–28 (1934).—The properties of barium carbonate, its general effect in glass melts, and its use in the production of (1) semicrystal, (2) hollow glassware, (3) pressed glass, (4) special glass (optical, scientific, electric insulation, illuminating, colored glasses, and enamels), (5) pane and plate glass, are discussed. Compositions of glasses are given. M.V.K.

Belgian folklore: objects in glass. ANON. *Verre & Silicates Ind.*, **5** [3], 44 (1934).—Examples of objects made from blown glass are given. Illustrated. M.V.K.

"Blue edge" when melting glasses with coke-oven gas: a glass or a gas defect? HERBERT LEHMANN. *Sprechsaal*, **67** [23], 343–45; [24], 360–61 (1934); abstracted in *Verre & Silicates Ind.*, **5** [15], 290 (1934).—The appearance of a blue edge when melting cup-shaped test and beaker glass with coke-oven gas is described. It was determined that the sulfur compounds of the gas and of the glass were not the reason for the defect. The formation of the edge is in direct relation to the surface alkalinity and, generally, to the alkalinity of the glass. The coke-oven gas absorbs more alkali from the outside glass than ordinary illuminating gas because of its high combustion temperature and high content of water. When the burning gas strikes the interior of the cup, it becomes saturated with sodium and being unable to extract it any longer, deposits it. Because of an irregular firing of alkalis, differences in stresses appear between the inner and outer sides of the glass; these cause fissures and a contraction of the inner sides. The fissures and contraction are visible macroscopically as a mat, bluish-white edge. Illustrated. M.V.K.

Bubbles found in the glass melt. ANON. *Glashütte*, **64** [14], 231–33 (1934).—The origin of bubbles in the glass melt, including (1) gas bubbles, (2) oxide bubbles, and (3) salt bubbles is discussed. References are given. M.V.K.

Chemical durability. JAMES BAILEY. *Glass Ind.*, **15** [8], 171–73 (1934).—Tests to measure the chemical durability of glass may be divided as follows: (1) tests of the original surface as manufactured; (2) tests of an especially prepared surface such as a ground and polished surface; (3) tests of a crushed sample in which the surfaces are primarily those of the cracked main body of glass. The methods of testing may consist of (*a*) boiling in distilled water for a definite time at atmospheric pressure, (*b*) subjecting the samples to vapor at a definite temperature, (*c*) subjecting them to saturated steam at elevated temperature and pressure, (*d*) using dilute solutions of alkali or acid instead of water. Results may be evaluated by (1) determining the change in weight of the sample before and after testing, (2) determining the alkali liberated by titration, (3) determining the material dissolved by evaporating to dryness and weighing, and (4) visual examination of the surface. In general, the following changes increase the chemical durability of the glass: (1) reduction of the alkali, (2) increase in the lime. (3) addition of alumina, (4) addition of small amounts of B_2O_3 and BaO. If the cost of the batch will permit, PbO may be substituted for lime and the alkali reduced, resulting in a more durable glass for the same degree of softness. Zinc oxide is a powerful stabilizing compound. If the alkali is made up of both soda and potash a more resistant glass results. E.J.V.

Condensable vapors in a tank furnace melting a saltcake batch. J. S. GREGORIUS AND W. A. MAHAFFEY. *Jour. Amer. Ceram. Soc.*, **17** [10], 307–309 (1934).

Corrosion figures of glass. JEAN HERBERT. *Compt. rend.*, **199** [5], 369–71 (1934).—If glass is attacked by hydrofluoric or fluosilicic acid certain corrosion figures are formed on the surfaces which recent investigations show to be crystals of sodium and calcium fluosilicate. Conditions under which these crystals are formed are described. M.H.

Cost of alumina from feldspar. S. R. SCHOLES. *Glass Ind.*, **15** [8], 174 (1934).—To demonstrate the economy of feldspar as a source of alumina for glass production as compared with other materials of equal purity, S. presents cost data, crediting against the cost of the feldspar the value of the silica sand and soda ash replaced by it and comparing the cost per pound of alumina with the same factor for other materials. Other materials are discussed as to suitability for use in glass production. E.J.V.

Crystallization of pseudowollastonite by devitrification of glass. MARCEL BELLIÈRE. *Verre & Silicates Ind.*, **5** [9], 162–67 (1934); translated in *Glass Ind.*, **15** [8], 178–81 (1934); for abstract see *Ceram. Abs.*, **13** [4], 84 (1934). E.J.V.

Crystallization and striation of glass manufactured on Fourcault machines. L. K. KOVALEV. *Keram. i Steklo*, **10** [7], 35–38 (1934).—A detailed discussion of reasons promoting the crystallization and striation of sheet glass produced on Fourcault machines is given. Measures to insure the production of sheet glass of higher quality and changes in the Fourcault machine are enumerated. The smaller the inclination to crystallization of the glass, the less striated and wavy it will be. See also *Ceram. Abs.*, **12** [1], 14 (1933). M.V.K.

Determining the flowing structure in glass. W. EITEL. Presented at the fall, 1933, meeting of the German Glass Trade; from *Referatkartei der Silikatliteratur*, No. 8 (1934). M.C.S.

Diffraction of X-rays in glass. B. E. WARREN. *Phys. Rev.*, **45** [10], 657–61 (1934).—A method is developed for calculating the scattering of X-rays in an amorphous solid. This is applied to the diffraction patterns of glass. In vitreous SiO_2, each Si is tetrahedrally surrounded by 4 oxygens at a distance Si − O = 1.60 Å. Each O is shared by two such tetrahedral groups. The result is a random

network which does not repeat at regular intervals. Accordingly, it is noncrystalline and glass is an amorphous solid. This term is preferable to "undercooled liquid," since amorphous solid implies the absence of a definite melting point and indicates that the atoms in glass have permanent neighbors; the latter is a characteristic of the solid state. Scattering curves calculated for vitreous SiO_2 and GeO_2 on the basis of this picture of the glassy state agree well with the experimental curves. J.L.G.

Durability of glass. ANON. *Glass Ind.*, **15** [8], 187–91 (1934).—The first divisions of a bibliography on chemical durability of glass, (1) weathering of glass, (2) tests and methods of testing, and (3) action of chemicals and water on glass, are presented. E.J.V.

Effect of alumina on devitrification of lime glasses. DONALD E. SHARP. *Nat. Glass Budget*, **50** [10], 13 (1934).—A study of various glasses was made in an effort to determine some relationship between the alumina content and the devitrification tendency of glass. Commercial lime glasses were made the basis of the investigation and in one case the alumina was substituted directly for lime while in another case the alumina was merely added to the original composition. In general, between 1 and 2% Al_2O_3 lowers the crystallization temperature and the tendency of divitrification of most soda-lime glasses. M.C.S.

Elastic after-effect in glass. K. H. BORCHARD. *Sprechsaal*, **67** [20], 297–99 (1934).—Deformation processes preceding rupture were investigated on glass rods and bottles. The dependence of the temporary after-effect phenomena on various influences is described. The dependence of the rupture due to deformation on time is characteristic for the glass concerned and the other hypotheses. Rupture is said to occur at the moment the temporary deformation curve cuts through the rupture expansion curve. M.V.K.

Ennobling sheet glass. F. H. ZSCHACKE. *Glashütte*, **64** [12], 195–97; [15], 243–44 (1934).—Methods for ennobling or refining sheet glass are (1) thermal after-treatment of the glass to change its shape, (2) mechanical treatment of the glass surface by grinding and polishing, (3) chemical treatment of the surface through etching, firing of metal oxides or glass colors, lustering and irisating, glazing, (4) coating the glass surface with metal layers, such as silvering and coating with gold, platinum, or copper, and (5) the manufacture of safety glass. The methods mentioned are briefly discussed. M.V.K.

Essentials of glass technology based on American practice. XII. S. R. SCHOLES. *Ceram. Ind.*, **23** [3], 154–56 (1934).—The region of commercial glass composition is essentially that of the compound $Na_2O{\cdot}3CaO{\cdot}6SiO_2$, and temperatures in this region range from 725 to 1060°C. Many glasses contain part or all of their alkali as K_2O, but its use is limited by its high cost. Most glass is essentially of the soda-lime-silica type, modified by the inclusion of small percentages of other oxides. The characteristics and compositions of optical glasses are discussed. From the viewpoint of phase equilibrium, glass is to be considered as a liquid which has passed through its freezing point or range without crystallizing, and whose viscosity has increased until it has the physical properties of a rigid solid. For Part XI see *Ceram. Abs.*, **13** [10], 253 (1934). E.J.V.

Fundamentals in the application of vitrifiable colors. V. H. REMINGTON. *Ceram. Ind.*, **23** [3], 144 (1934).—Vitreous glass enamels, or glass colors, are essentially low fusing glasses of lead borosilicate composition. A glass enamel is termed "hard" or "soft," depending upon the amount of heat required to fuse it to the glass. Glass enamels may be applied by spraying, banding, stamping, dusting, or printing. The preparation of the colors for use with each of these processes is discussed. The silk screen process method of reproducing either single or multiple color designs largely used for decorating glass is described. Illustrated. E.J.V.

Glass manufacture in China. ANON. *Glashütte*, **64** [25], 419–20 (1934).—A brief review is given of glassware manufactured and raw materials used. M.V.K.

Glassmelting under reduced pressure. M. A. BESBORODOV. *Verre & Silicates Ind.*, **5** [11], 202–205 (1934).—The chemical analysis of the melt indicates that the decomposition of carbonates occurs at a temperature below 500° and is completed between 700 and 900°. The important decrease of the SiO_2 proportion contained in semiliquid melts at 900° and over corresponds to the formation of complex siliceous compounds insoluble in H_2O. The process of the formation of the glass is practically the same when melting under reduced pressure (50 mm. Hg) or normal pressure (760 mm. Hg). The amount of CO_2 is much less, however, when melting under reduced pressure. The index of refraction of the vitreous part varies between $n = 1503$ and $n = 1530$. There is no relationship between the value of these indices and factors such as temperature or pressure. All of the melts contain quartz grains except those obtained at 1300°. The microscopic examination of thin sections shows a reduction in size and number of unmelted particles with increased temperature. At high temperature the quartz grains become smaller and more round. There is no relationship between the proportion of unmelted particles and pressure. Vitreous melts obtained at high temperature have the least number of bubbles. These results show that melting under reduced pressure does not ameliorate the quality of the final product in a marked way. M.V.K.

Glass in modern architecture. A. SARTORIS. *Riv. Int. di Ing. San. ed Urb.*, 3–4, 73–76 (1933); abstracted in *Bibliografia Italiana* [Series C], **7** [3–4], 24 (1934).—Considering glass as a material which contributes greatly to the general appearance of modern buildings, S. discusses some of the principal uses of glass in modern architecture. H.F.V.

Glass paneled service station for Shell Eastern Petroleum Products Co. ANON. *Ceram. Ind.*, **23** [3], 125 (1934).—Illustrated. E.J.V.

Glass products depict history of industry. ANON. *Bull. Amer. Ceram. Soc.*, **13** [9], 233 (1934); *Ceram. Ind.*, **23** [2], 66 (1934); *Glass Ind.*, **15** [7], 153 (1934).—Glassware made by the Egyptians 2000 B.C. and finest examples of the glassware of all ages from the collection of the Toledo Museum of Art are shown in the glass block building of the Owens-Illinois Glass Co., Toledo, Ohio, at the Century of Progress. Illustrated. E.J.V.

Glass wool for insulating mats. C. A. ROBAK. *Ind. Eng. Chem., News Ed.*, **12** [15], 273 (1934).—The produc-

tion of glass wool by a Swedish company is essentially as follows: The melted glass runs down upon a disk which rotates with great velocity. By action of the centrifugal force, the glass is disintegrated into a mass of extremely fine threads. A current of air is blown downward around the edge of the rotating disk, carrying the formed glass wool down upon a cutting and transporting apparatus, by means of which the product is continuously carried away for further working. The fineness of the glass threads can be controlled within certain limits by regulating the temperature of the melted glass and the amount of glass fed upon the rotating disk per unit of time. By the method described much finer threads can be produced than by other methods. Insulating mats manufactured from the glass wool by pressing and sewing contain only approximately 4% of glass by volume and weigh only 100 to 110 kg./cu. m. F.G.H.

German hollow glass industry. W. KALVERAN. Presented at the fall, 1933, meeting of the German Glass Trade; from *Referatkartei der Silikatliteratur*, No. 3 (1934). M.C.S.

Indium glass. W. S. MURRAY. *Ind. Eng. Chem.*, **26** [8], 903–904 (1934).—The addition of indium sesquioxide to a glass mixture containing sulfur colors the glass yellow in proportion to the amount of indium sesquioxide used. This color appears to be developed by the interaction of indium sesquioxide as the glass is being made, because adding the indium sulfide (In_2S_3) to the glass-forming mixture does not produce the same result. The color is progressive, from light canary to dark tangerine-orange. F.G.H.

Iridescence of old glasses. Formation of Liesegang layers in the glass in contact with solutions of bicarbonates by rhythmic precipitation of calcium carbonate. MARCEL GUILLOT. *Compt. rend.*, **198** [24], 2093–95 (1934).—The iridescent patina on antique glasses is generally considered to consist of the superposition of numerous thin films of silica which optically are quite distinct from one another. It was attempted to form these films artificially in the laboratory; several methods are described. It seems probable that they are formed by a process similar to that of the Liesegang rings where the glass plays the part of the gelatin. At the contact of a saturated solution of alkalinic bicarbonate the CO_3 ions enter the glass and cause a stratified precipitation of CO_3Ca while the Ca^{++} ions diffuse in the inverse sense. The glass is thus impoverished in Ca so that it becomes more permeable to water and facilitates passage of Na^+ ions in solution which can take place only in too alkaline solutions; iridescence appears rapidly in saturated bicarbonate solutions, slowly in carbonate solutions, and not at all in concentrated soda solutions. M.H.

Manufacture of Triplex glass. R. D. *Verre & Silicates Ind.*, **5** [12], 221–25 (1934).—The development of the safety glass industry, the present manufacture of Triplex glass, and its testing are described. See also *Ceram. Abs.*, **13** [10], 257 (1934). M.V.K.

Measurement of the transmission of colored glasses. H. W. LEE. *Glass Ind.*, **15** [8], 175–77 (1934).—For transmission measurements the required equipment consists of (1) a source of light, (2) a means of splitting the light into its constituent colors, and (3) a means of measuring the light. The light splitter is called the spectrometer and consists of a collimator, a prism, and a telescope. The wave-length of the emerging light is determined by a monochromator. The amount of light transmitted by a glass is usually measured by dividing a beam of light into two beams which are reunited in juxtaposition in the eye, which thus is able to judge of any inequality of brightness. The intensity of the two beams is adjusted to quality and then the glass is inserted in one beam. This upsets the balance so that the other beam must be diminished in intensity by a measurable amount until the balance is restored. The percentage absorption of the colored glass is then equal to the percentage diminution of the comparison beam. Methods of standardization of colored glasses are described. Illustrated. E.J.V.

Methods of working glass. A. GRADENWITZ. *Industria*, **12**, 256–57 (1932); abstracted in *Bibliografia Italiana* [Series C], **6** [5–6], 22 (1933).—G. discusses the turning, drilling, and planing of glass (using the alloy Widia) and the working of porcelain. H.F.V.

Mineral precipitations in glasses. MAURICE BILLY AND MARC-ANTOINE FOEX. *Compt. rend.*, **199** [1], 57–59 (1934).—Experiments on the precipitation of metal oxides in glass showed analogy with the dissolution of the same oxides in aqueous alkaline solutions, *e.g.*, at about 100°C, an appreciable dissolution of NiO is obtained with $100MH_2O$ and $20MNa_2O$; SiO_2, B_2O_3, or P_2O_5 play the part of H_2O, and the salts obtained play the part of hydrates. It was found that Au and Ag are soluble in alkaline glasses only in the presence of O; without B_2O_3, P_2O_5, or SiO_2, Au is not dissolved. If Au or Ag glasses are melted at a high temperature and rapidly cooled they are colorless and transparent; with slow cooling, they give metallic crystals even in the colloidal state and become colored. Metallic oxides and salts can be precipitated as oxides, as salts only, and as salts for less alkali-rich glasses and as oxides for alkali-rich glasses. These conditions are discussed in detail. M.H.

Obtaining "frost flower effects" on glass. ANON. *Glashütte*, **64** [9], 150–51 (1934).—To obtain "frost flowers" on glass, the glass sheet is first ground with a sandblast and then dusted, and one or several coats of bone glue are uniformly applied. On drying, the bone glue shrinks and tears away glass particles from the surface of the sheet. The kind of flower effect obtained depends on the way the bone glue is applied and the drying. M.V.K.

Origin and appearance of glass technical manufacturing defects during various stages of glass production. ANON. *Sprechsaal*, **67** [25], 375–77 (1934). M.V.K.

Polishing media for glass. W. O. *Diamant*, **56** [20], 232 (1934).—The addition of hygroscopic salts, such as calcium or magnesium chloride, to polishing agents (which are mixed with water), *e.g.*, iron oxide or similar materials, is recommended. M.V.K.

Preparation of microscopic glass spheres. S. SKLAREW. *Ind. Eng. Chem., Anal. Ed.*, **6** [2], 152–53 (1934).—Microscopic glass spheres were prepared by floating powdered glass on air through the combustion zone of gas-fired blast lamps. Various uses of the spheres are described. Illustrated. F.G.H.

Progress of the glass industry in 1933. OSCAR KNAPP. *Glashütte*, **64** [20], 315–16 (1934).—A brief review is given of the latest researches dealing with (1) structure of glasses, (2) constitution of glasses and the theoretical bases of glass coloring, (3) structure of zinc-borate glass, (4) structure of cobalt glass, (5) definition of glass, (6) thermal expansion of glass, (7) behavior of oxides under high oxygen pressure, (8) reaction velocity between silica and sodium carbonate at various temperatures, (9) reaction between lime and silica, (10) 3-component system Na_2SiO_3–$Na_2Si_2O_5$–$NaAlSiO_4$, (11) reduction and oxidation of manganese silicates, and (12) beryllium glasses. Bibliography. See also *Ceram. Abs.*, **13** [7], 176 (1934). M.V.K.

Report of the Joint Committee on Illuminating Glasses of the Glass Division, American Ceramic Society, Illuminating Engineering Society, and Illuminating Glassware Guild. H. H. BLAU. *Bull. Amer. Ceram. Soc.*, **13** [9], 219–23 (1934).

Stresses in wire glass arising from the wire. FRANK W. PRESTON. *Jour. Amer. Ceram. Soc.*, **17** [10], 310–11 (1934); see also *Ceram. Abs.*, **10** [7], 485 (1931).

Summary of a course of study of glassmaking. R. D. *Verre & Silicates Ind.*, **5** [9], 169–71; [11], 211–12; [15], 287–90 (1934).—Details of the manufacture of various kinds of industrial glasses are given. Illustrated. For previous articles see *Ceram. Abs.*, **13** [9], 234 (1934). M.V.K.

Technique of illumination. M. PIRANI. *Physik*, **2**, 127–40 (1934).—This is a review of the present knowledge of illumination. The principles for choosing a light source for a given purpose, such as illuminating a shop, etc., are outlined. Lamps using temperature radiation of solid wires, etc., and gas discharge tubes emitting monochromatic light are described. Gas discharge tubes for plant work are available in many different colors. W.M.C.

Ternary diagrams of viscosity for glasses. N. V. SOLOMIN. *Keram. i Steklo*, **10** [7], 32–34 (1934).—The building of ternary diagrams to determine the viscosity curve of glasses of various compositions is discussed, and its application is explained by examples. M.V.K.

Thermal endurance of glass. KOZO TABATA AND TARO MORIYA. *Jour. Amer. Ceram. Soc.*, **17** [10], 313 (1934).—Changes in the original paper are noted (*Ceram. Abs.*, **13** [3], 56 (1934)).

Three-ply or five-ply toughened glass or toughened glass combination as safety glass. FRITZ OHL. *Sprechsaal*, **66** [48], 820–22 (1934).—Comparative data are given on the mechanical strength of safety glass (machine glass and toughened glass) with 3 and 5 intermediate layers of celluloid and polymerisate of acrylic acid. Several German patents are discussed. M.V.K.

Viscosity of iron slag. K. ENDELL. *Stahl & Eisen*, **54** [25], 663 (1934).—A method for measuring viscosities of slag, glass, etc., is described. A crucible containing the substance to be investigated is placed in an electric furnace and heated to a constant temperature. A ball connected with a rod is inserted in the melt, ball and rod being made of platinum or fused alumina. The ball and rod are connected over a thread to a lever with counterweight. The time for moving the ball upward in the melt over a given distance is measured. The viscosity of the glass or slag for that particular temperature of the experiment is computed from the time. The temperature range of the apparatus is from 1100 to 1500°C, and the working range extends from 1 to 100,000 g./cm. sec. The same apparatus may be used for measuring the density of molten glass or slag. It has been found that the density of glasses will decrease with increasing temperature, whereas that of slags will first increase and then decrease. Absolute viscosities may be calculated if the densities are available. Measurements are being carried out for coal slags. Great differences have been detected for different types of coal. W.M.C.

PATENTS

Appparatus for case hardening glass. L. V. BLACK (Pittsburgh Plate Glass Co.). U. S. 1,970,730, Aug. 21, 1934.

Apparatus for scoring and snapping flat glass automatically. F. B. WALDRON (Pilkington Bros., Ltd.). U. S. 1,972,210, Sept. 4, 1934.

Apparatus for making glassware. K. E. PEILER (Hartford-Empire Co.). U. S. 1,971,352, Aug. 28, 1934.

Feeding glass tubes to a machine for shaping or working them. J. DICHTER. Brit. 415,202, Aug. 29, 1934.

Forehearth for glassmelting furnaces and method of conditioning molten glass. THOMAS WARDLEY (Hartford-Empire Co.). U. S. 1,970,113, Aug. 14, 1934.

Glass cutting apparatus. E. J. BRASSEUR AND G. J. RICE (Libbey-Owens-Ford Glass Co.). U. S. 1,970,930, Aug. 21, 1934.

Glassware forming machine. R. G. ALLEN (Owens-Illinois Glass Co.). U. S. 1,970,792, Aug. 21, 1934.

Groove grinding machine. CHRISTOPHER BROWN (Pittsburgh Plate Glass Co.). U. S. 1,970,733, Aug. 21, 1934.

Glass handling apparatus. H. S. HEICHERT (Pittsburgh Plate Glass Co.). U. S. 1,970,749, Aug. 21, 1934.

Glass pressing machines. PILKINGTON BROS., LTD. Brit. 414,332, Aug. 9, 1934.

Headlight lens. C. H. J. BURGER. U. S. 1,969,714, Aug. 14, 1934.

Machine for blowing glass articles in molds. L. D. SOUBIER (Owens-Illinois Glass Co.). U. S. 1,972,464, Sept. 4, 1934.

Machine for cutting sheets of glass, etc. E. A. ROSIN (Libbey-Owens-Ford Glass Co.). U. S. 1,970,919, Aug. 21, 1934.

Manufacture of fused bifocal lenses. EDWARD CULVER AND A. H. EMERSON (United Kingdom Optical Co., Ltd.). U. S. 1,971,394, Aug. 28, 1934.

Manufacture of laminated nonsplintering glass. W. D. SPENCER AND IMPERIAL CHEMICAL INDUSTRIES, LTD. Brit. 414,073, Aug. 9, 1934.

Means and method for controlling the temperature and condition of molten glass in forehearths. W. T. HONISS (Hartford-Empire Co.). U. S. 1,970,094, Aug. 14, 1934.

Means for feeding molten glass. JAMES BAILEY (Hartford-Empire Co.). U. S. 1,970,354, Aug. 14, 1934.

Method and apparatus for making footed glassware.

H. R. SCHUTZ (Libbey Glass Mfg. Co.). U. S. 1,972,717, Sept. 4, 1934.

Method and apparatus for making glass with salt. H. A. WADMAN (Hartford-Empire Co.). U. S. 1,970,112, Aug. 14, 1934.

Method of calking laminated glass. E. H. HAUX (Duplate Corp.). U. S. 1,970,748, Aug. 21, 1934.

Preformed structural unit and method of making. J. C. MACILDOWIE (Johns-Manville Corp.). U. S. 1,970,328, Aug. 14, 1934. A preformed structural unit comprises a facing sheet of glass, a backing sheet of stonelike material, and a layer of yieldable material disposed between the sheets and adhered to them to form a unitary article.

Process and apparatus for tempering glass sheets. BERNARD LONG (American Securit Co.). U. S. 1,971,268, Aug. 21, 1934.

Protection of molten baths. J. S. GUMMERT AND J. E. HUTCHINSON (Pennsylvania Salt Mfg. Co.). U. S. 1,970,136, Aug. 14, 1934. A method of insulating and protecting molten baths from oxidation comprises adding to the bath a material which contains free aluminum oxide as its predominant constituent.

Reflecting system applicable to signals, signs, etc. CORNING GLASS WORKS. Brit. 415,003, Aug. 22, 1934.

Sandblasting apparatus. A. W. MIKSCH (Pittsburgh Plate Glass Co.). U. S. 1,970,762, Aug. 21, 1934.

Sheet glass cutting apparatus. J. L. DRAKE (Libbey-Owens-Ford Glass Co.). U. S. 1,970,932, Aug. 21, 1934.

Tile. G. F. MATTMAN (Cincinnati Advertising Products Co.). U. S. 1,970,759, Aug. 21, 1934. A colored tile comprises an originally transparent glass body having color on one face thereof and perceptible through the body, a coating of neutral shade relative to the color and applied over the color to render the body opaque, and a final coating applied over the first coating and forming the rear face of the tile, the final coating being adapted to preclude seepage of mastic or other tile-positioning material into contact with the first coating.

Transferring apparatus for incompletely solidified glass bottles, etc. LÉON LHOEST. U. S. 1,971,110, Aug. 21, 1934.

Ultra-violet transmitting glass. KITSUZO FUWA (General Electric Co.). U. S. 1,971,309, Aug. 21, 1934. A method of manufacturing glass capable of transmitting ultra-violet radiation consists in adding a halogen compound and a small quantity of an alkaline tartrate to the glass batch.

Structural Clay Products

Brick sewer in Connecticut compares favorably with other types. ANON. *Brick Clay Rec.*, **85** [2], 54–56 (1934).—Cost figures of the first brick sewer in New Britain, Conn., indicate that brick-sewer construction is economical not only because of its everlasting life and other advantages, but from a standpoint of actual comparative costs. Using CWA labor exclusively, 1958 linear feet of 26-inch, 2-ring sewer were completed at a cost of $5.20/ft. of finished sewer. Illustrated. E.J.V.

Clay manufacturers find new market using waste clay for mortar mix. H. R. STRAIGHT. *Brick Clay Rec.*, **85** [2], 51–52 (1934).—Iowa clay products manufacturers have developed a market for a fine ground raw clay which is generally known as mortar mix. Tests were made to compare mortar mix directly with lime in mortars of different proportions, covering tensile, compressive, adhesive, or bonding strengths, water penetration or porosity, resistance to freezing and thawing, slakability, and dryness as prepared for packing. All tests showed that the best mortars from a standpoint of necessary characteristics were secured in a 3 to 1 mix of sand and cement in which 25% of the cement had been replaced with mortar mix. With this mixture the strength of the mortar mix-cement-sand mixture was slightly in excess of a similar lime-cement-sand mix of the same proportions, except in the compressive strength which was practically the same. A list of advantages pointed out by masons and contractors is given. The most desirable product is prepared from defective dried ware. E.J.V.

Lamination of brick. A. GALLASCH. *Tonind.-Ztg.*, **58** [45], 537–39 (1934).—The high cost of clay products is chiefly accounted for by the large quantity of defective raw and fired products. Lamination is caused chiefly by (1) wrong selection of raw materials, (2) unsuitable machines, (3) wrong construction of machines, (4) too rapid drying, and (5) unsatisfactory firing process. M.V.K.

Occurrences of nitrates in wall brick. WALTER MARSCHNER. *Tonind.-Ztg.*, **58** [38], 465–66 (1934).—The small quantities of saltpeter in brick are harmless, and numerous investigations show that saltpeter is not present in brick efflorescences. Nitrates are not entirely eliminated by firing. The determination of the salt content in brick is briefly dealt with. M.V.K.

Steel vs. brick. Use of steel construction as affecting the brick trade. H. M. DE COLLEVILLE. *Brit. Clayworker*, **43** [508], 143–44 (1934).—D. discusses brick substitutes, reduction of the normal thickness of brick, disadvantages of steel, attacks on brickwork, and factors for consideration in connection with the use of steel in building construction. R.A.H.

PATENTS

Apparatus for loading or piling brick, etc. R. R. SUTCLIFFE. Brit. 414,081, Aug. 9, 1934.

Brick wall and waterproofing means therefor. A. L. LARSON. U. S. 1,970,326, Aug. 14, 1934.

Cavity brick for building purposes. J. J. HINE AND W. A. FOX-STRANGWAYS. Brit. 414,940, Aug. 22, 1934.

Preparation of material for making brick, etc. T. C. FAWCETT, LTD., D. L. FAWCETT, AND A. E. BOTTOMLEY. Brit. 415,243, Aug. 29, 1934.

Refractories

Action of coal ash on refractories. G. W. M. Rees. *Eng. Boiler House Rev.*, **47** [10], 668–70 (1934); abstracted in *Sprechsaal*, **67** [30], 450 (1934). M.V.K.

Changes in the inner structure of siliceous materials by heat treatment. I. X-ray studies of natural minerals. T. Nakai and Y. Fukami. *Jour. Soc. Chem. Ind.* [Japan], **37** [5], 283–84*B* (1934).—No marked changes were found in minerals when heated up to 1000°, while in those heated between 1000 and 1500° conspicuous changes were observed, cristobalite being formed without tridymite. The change in the inner structure of minerals is much more affected by the kind of mineral or its original structure. In the change of structure, such as quartz to cristobalite, amorphous silica to cristobalite, or tridymite to cristobalite, the impurities contained in the sample have a marked effect in accelerating these transformations. M.V.K.

Corrosion of glass furnace blocks. B. F. Kuzmich and M. G. Stepanenko. *Keram. i Steklo*, **10** [6], 22–28; [7], 24–28 (1934).—Details are given of examinations of several glass tank furnaces and of the degree of corrosion of the blocks. Illustrated. M.V.K.

Destruction of refractory masonry in boiler furnaces. W. Wassermann. *Feuerungstechnik*, **22** [6], 70–72 (1934). M.V.K.

Dimensional changes of clayware during firing. III. Testing method for refractory mortars. Tosaku Yoshioka, Taizo Horie, and Junitzu Karashima. *Jour. Soc. Chem. Ind.* [Japan], **37** [4], 172*B* (1934); for Part II see *Ceram. Abs.*, **12** [12], 435 (1933). M.V.K.

Effect of preliminary grinding of quartz sand on the quality of Dinas brick. P. P. Budnikoff and N. S. Kossian. *Keram. i Steklo*, **10** [7], 29–31 (1934).—It was found that the macrostructure of Dinas brick containing ground quartz sand is uniform, dense, and of a pale cream color. The isotropic base (glass) is intensively interlaced by felt-like nettings of anisotropic crystalline needles of tridymite with inclusions of grains of calcium and iron metasilicates. Fissures between the quartz grains are filled up with glass. No cristobalite was found. The chemical analysis shows that the silica content is somewhat lowered in some brick. The CaO content is not higher than 3.92% and has no effect on the refractoriness and on the deformation temperature of the brick. The mechanical strength of Dinas brick decreases with the increased amount of sand. The water absorption and volume porosity increase with the quantity of sand used. The refractoriness of the Dinas brick is cone 32 (1710°). The specific gravity increases with the amount of sand. Up to 35% sand can be used without lowering the properties. An addition of molasses to the mix is necessary. M.V.K.

Electrical lubrication of hand-molded refractory shapes. J. Otis Everhart. *Jour. Amer. Ceram. Soc.*, **17** [10], 312–13 (1934).

Extraction of alumina from its silicates by sulfuric acid. Yogoro Kato, Koemon Funaki, and Ryortiro Yasima. *Jour. Soc. Chem. Ind.* [Japan], **37** [4], 169–70*B* (1934).—Aluminium silicate is decomposed by concentrated sulfuric acid in solid state. The aluminium sulfate is extracted from the product with water. Methods for obtaining pure $Al_2(SO_4)_3 \cdot 18H_2O$ are developed from which pure aluminium hydroxide can be produced. M.V.K.

Grog clay "SN" of the clayworks of Adolf Gottfried of Fonsau-Wildstein at Eger, Bohemia. Gustav Kopka and Friedrich Zapp. *Sprechsaal*, **67** [18], 263–65 (1934). M.V.K.

Investigation of forms of carbon by means of cathode ray diffraction. M. Miwa. *Sci. Repts. Tôhoku Imp. Univ.*, **23** [2], 242–58 (1934).—Various forms of carbon were studied. Most results show a good agreement with those obtained by means of X-rays. The so-called amorphous carbon was found to be a form of graphite of very small grain size. The magnetic susceptibility of the samples is nearly proportional to the grain size of amorphous carbon. W.M.C.

Iron oxide effect on the firing of grog. Eberhard Goebel. *Tonind.-Ztg.*, **58** [48], 572 (1934).—The behavior of clay, especially its porosity with increased temperature between 900 and 1500°, varies greatly and is not in direct relation to the iron oxide content. Curves are given showing the behavior of different German plastic and lean clays. Lowering of the specific gravity is proportionate to an increase in volume of the materials and, through this, an increase in porosity. M.V.K.

Manufacturing silica products. Gr. W. *Tonind.-Ztg.*, **58** [52], 625–26 (1934).—The effect of (1) preparation of the mix, (2) moisture content, (3) molding, and (4) drying of the finished silica products is briefly discussed. M.V.K.

Mullite in clay refractories. Tosaku Yoshioka, Taizo Horie, and Junitzu Karashima. *Jour. Soc. Chem. Ind.* [Japan], **37** [4], 171–72*B* (1934).—Refractories of the SiO_2–Al_2O_3 system were studied as to their mullite content using a new HF method, and the isolated mullite grains were tested under microscope. From the forms of crystals, the nature of the raw materials used could easily be determined. Fine crystal needles of mullite show that it is of secondary nature formed during firing, while the presence of mullite fragments shows that primary mullite, such as fused or transformed mullite, was used as the raw material. The mullite content varied from 90 to 20% in refractories. The HF method is described. M.V.K.

Refractories for boiler furnaces. Anon. *Eng. Boiler House Rev.*, **47** [3], 154–56 (1933); abstracted in *Sprechsaal*, **67** [26], 390 (1934). M.V.K.

Refractories with chrome base. Maurice Déribéré. *Rev. mat. constr. trav. pub.*, No. 297, pp. 101–104*B* (1934).—A brief review is given of world deposits of chromite. An analysis and characteristics of chromite blocks are given. Chromite brick are employed instead of magnesia brick in Siemens-Martin electric furnaces and those fusing copper and other metals. Data on German chromite brick are given. Siemensite cast brick, a mixture of chromite, magnesite, and bauxite (20 to 40% Cr_2O_3, 25 to 45% Al_2O_3, and 18 to 30% MgO), do not deform at 1800° with a load of 2 kg./sq. cm ; their density is 3.2 to 3.4; coefficient of dilatation is 1.2 to 1.4% up to 1200°. The thermal conductivity is little higher than that of

magnesia brick. The product is neutral and is resistant to acid and basic slag. A table with comparative properties of chromite, magnesia, and silica brick and a literature index are given. M.V.K.

Refractory products. M. BELLARD. *Jour. four élec.*, **43** [8], 291–92 (1934).—B. outlines the properties of brick made from silica, clay, high alumina clays, magnesia, chrome, and zircon. G.R.S.

Super-refractories for the iron and steel industry. W. F. ROCHOW. *Iron & Steel Eng.*, **11** [8], 296–300 (1934); see also *Ceram. Abs.*, **13** [6], 151 (1934). E.J.V.

Testing machine for refractory materials. ANON. *Messtechnik*, **10** [7], 127–28 (1934).—A new apparatus, devised by D. Petit, for determining (1) the melting point, (2) softening under load at high temperature, (3) permanent and reversible expansion, (4) after-shrinkage, and (5) resistance to variations of temperature of refractories is described in detail. Illustrated. M.V.K.

BULLETINS

Insulation of industrial furnaces and ovens. JOHNS-MANVILLE CORP., New York. Reviewed in *Foundry*, **62** [4], 77 (1934).—This booklet describes and illustrates a wide variety of insulation methods as applied to industrial furnaces. F.G.H.

Sil-O-Cel C-22 brick. JOHNS-MANVILLE CORP., New York. Reviewed in *Ind. Eng. Chem., News Ed.*, **12** [12], 240 (1934).—This bulletin contains complete engineering information on insulating brick, including data on thermal conductivity, strength, permeability, expansion, and behavior at high temperature. F.G.H.

PATENTS

Arch brick. J. P. NEFF (American Arch Co.). U. S. 1,971,693, Aug. 28, 1934.

Boiler wall. C. V. HENDRICKSON (Metropolitan Engineering Co.). U. S. 1,971,312, Aug. 21, 1934. A boiler wall structure comprises an outer portion, tubes on the inner face of the latter, and a lining on the inner face of the tubes, the outer portion of the wall and the lining being tied together by ties loosely engaging the outer portion of the wall and the lining and passing between the tubes.

Furnace firebridge. A. FALDERBAUM. Brit. 414,970, Aug. 22, 1934.

Furnace wall. W. F. KEENAN, JR. (Foster Wheeler Corp.). U. S. 1,972,593, Sept. 4, 1934. C. E. LUCKE (Fuller Lehigh Co.). U. S. 1,972,100, Sept. 4, 1934. D. W. ROSS AND J. M. LAMBIE. U. S. 1,970,944, Aug. 21, 1934.

Manufacture of refractory materials and materials possessing heat and sound insulating properties. SOC. ITALIANA PIRELLI. Brit. 414,934, Aug. 22, 1934.

Means preventing passage of gas through refractory walls. L. A. MEKLER (Universal Oil Products Co.). U. S. 1,971,915, Aug. 28, 1934.

Process of recovering alumina from aluminous siliceous materials. A. W. SCHEIDT AND R. C. FOLGER (Electric Smelting & Aluminum Co.). U. S. 1,971,354, Aug. 28, 1934. A process of treating aluminous siliceous material comprises forming a furnace charge of such material mixed with calcium carbonate and alkali aluminate of low alumina content in substantially the molecular proportion of 1 mol. of silica to 2 mol. of calcium oxide and of 1 mol. of alumina to 1 to 1.7 mol. of alkali metal oxide, heating the charge to form a sinter, dissolving the alkali aluminate, separating a portion of the alumina therefrom, and returning the resulting alkali aluminate of low alumina content for reuse in the process.

Refractory brick. R. P. HEUER (General Refractories Co.). U. S. 1,969,751, Aug. 14, 1934. A method of making silica brick of high density consists in vitrifying the silica, crystallizing the vitrified silica, and subsequently forming the silica into brick.

Silica brick. R. P. HEUER (General Refractories Co.). U. S. 1,969,750, Aug. 14, 1934. A method of producing silica brick of volume stability and low porosity from a silica mineral containing quartz consists in preliminarily subjecting the mineral to a temperature above 1400°C until the specific gravity of individual crystalline particles is less than 2.38 and the porosity of individual crystalline particles is less than 18%, whereby the silica is pregrown and coalesced, and in subsequently interfitting into brick a mass of particles including as a predominant constituent pregrown coalesced silica particles.

Terra Cotta

Acid-stable stone linings for acid constructions in the celluloid industry. KRUSE. *Zellstoff & Papier*, No. 12, pp. 600–602 (1933); abstracted in *Chem.-Ztg.*, **57** [97], 961 (1933); *Tonind.-Ztg.*, **58** [37], 460 (1934).—K. deals with (1) the properties of acid-stable brick and cements, (2) requirements of the celluloid industry for lining materials, (3) advantages of ceramic linings over those of lead; (4) the products, Höchst and Asphit, and (5) the best linings. M.V.K.

Acoustic properties of building materials, using brief acoustic signals. F. SPANDÖCK. *Ann. Physik*, **20** [3], 328–44 (1934).—A loud-speaker emits a brief acoustic signal which strikes a microphone, the wall to be tested, and again the microphone. The reflection properties of the building material tested are derived from oscillograph records. Data are presented for several floor and ceiling materials. Further tests included acoustic properties of cloths and the influence of diffraction on reflection from small rectangular and circular areas. W.M.C.

Effect of de-airing on the fired properties of a terra cotta body. R. L. CLARE. *Bull. Amer. Ceram. Soc.*, **13** [9], 223–24 (1934).

Roofing tile from evacuated clay. A. C. HEIL. *Tonind.-Ztg.*, **58** [5], 51–52 (1934).—The formation of air blisters, bubbles, and layers due to occluded air is discussed in detail. The advantages of treating clay in vacuum presses are pointed out. Illustrated. See also *Ceram. Abs.*, **13** [7], 188 (1934). M.V.K.

Salt glaze. I. Reaction between silica and mixed vapor of water and sodium chloride. SEIJI KONDO AND

SHIN-ICHI SUGUKI. *Jour. Soc. Chem. Ind.* [Japan], **37** [4], 173*B* (1934).—Sodium chloride was heated from 900 to 1300° for 1 to 5 hr. in a nitrogen atmosphere containing steam and sodium chloride vapor. Transparent glassy materials produced were analyzed for their silica and soda contents. The effect on the reactions of quicklime and magnesia placed in the waste gases was studied. M.V.K.

Structural ceramics. FRITZ THEILMANN. *Bauwelt*, **16**, 384–86 (1934); abstracted in *Tonind.-Ztg.*, **58** [45], 545 (1934).—The development of structural ceramics for the last three years is discussed. M.V.K.

PATENTS

Flowerpot. DUNBAR LOCKWOOD (A. H. Hews & Co., Inc.). U. S. 1,971,075, Aug. 21, 1934.

Method and means for forming roofing tile. J. W. PEMBERTON AND R. B. KEELER. U. S. 1,972,312, Sept. 4, 1934.

Stoneware and other conduits for electric cables. ALBION CLAY CO., LTD., AND G. O. LAWTON. Brit. 415,189, Aug. 29, 1934.

Wall coping. G. M. SCHAULIN (Robinson Clay Products Co.). U. S. 1,972,819, Sept. 4, 1934.

White Wares

Investigation proves another case of faulty installation. ANON. *Keram. Tile Jour.*, **6** [6], 6 (1934).—Many tile installations fail prematurely due to faulty setting and poor judgment on the part of the tile setters. Improper mortars are often the basis of failure. M.C.S.

Modern plant for fine ceramics and its equipment. D.-R. SIMON. *Keram. i Steklo*, **10** [7], 14–23 (1934).—A description is given of modern methods and equipment used in the manufacture of wall tile, household ware, and cast sanitary faience ware. M.V.K.

Porcelain for insulators. M. KORACH. *Ellettrotecnica*, **21** [5], 89–97 (1934); abstracted in *Bibliografia Italiana* [Series C], **7** [5–6], 22 (1934).—K. discusses the results of experiments conducted from 1924 to 1932 in developing a superior type of insulating porcelain. A special fabrication procedure is described. H.F.V.

Raw materials for porcelain and faience. V. CHARRIN. *Verre & Silicates Ind.*, **5** [9], 167–68 (1934).—A brief review of French resources in kaolin, feldspar, and silica is given. M.V.K.

Replacing feldspar by nepheline syenite in mixes for insulators. L. OMININ. *Keram. i Steklo*, **10** [6], 31–33 (1934).—Experiments with mixes containing nepheline syenite instead of feldspar showed that (1) bodies containing nepheline syenite are satisfactory in their mechanical, thermal, and dielectric properties; (2) they are gray and are covered with small specks due to iron; (3) such insulators must be glazed with opaque colored glazes; (4) the sintering interval of these mixes is wide, while deformation on firing is comparatively low. M.V.K.

Streaks in ceramic cast mixes. K. PFEFFERKORN. *Sprechsaal*, **67** [27], 401–405 (1934).—Formation of streaks depends on (1) pressure and (2) alkali content (Na_2CO_3). The greater these factors, the larger is the formation of streaks. This formation is due to a local separation into component parts of the slip by electrochemical processes. The separation is the most intensive when the clay substance molecules are very small and are affected by Na-ions. This fact explains the observation that raw materials liquefied with soda produce fissures on drying, while clays and kaolins liquefied with water show only weak streaks. The occurrence of streaks in filter-press cakes and in deep clay beds confirms the effect of pressure. Manufacturing defects favoring the formation of streaks are discussed. Illustrated. M.V.K.

BOOKS AND BULLETIN

Ceramic Materials for High-Frequency Technique (Keramische Baustoffe für die Hochfrequenztechnik). ERICH SCHWANDT. Hachmeister & Thal, Leipzig, 1933. 50 illustrations. 3.00 Rm. Reviewed in *Sprechsaal*, **67** [27], 414 (1934).—The book discusses the following points: (1) requirements of insulating materials in the high-frequency technique, (2) properties of insulating materials used for high-frequency purposes, (3) ceramic materials, (4) steatite mixes and their specific properties, (5) production of ceramic parts and their working, (6) ceramic parts of receivers, (7) ceramic materials in measuring apparatus, and (8) review of literature. M.V.K.

Insulators. ANON. *American Lava Corp. Bull.*, No. 34; *Ind. Eng. Chem., News Ed.*, **12** [12], 240 (1934).—Precision insulators made from lava, Alsimag, alumina, beryllia, and magnesia are discussed. F.G.H.

Manufacture of Porcelain Ware (Proizvodstvo farforovuikh izdelii'). M. V. FLEROV. Goskhimizdat, Leningrad, 1933. 183 pp., 43 illustrations. Reviewed in *Keram. i Steklo*, **10** [7], 39 (1934).—The largest part of this book contains a detailed description of specific methods, observation of which is necessary in the process of molding the ware and in working of raw materials and the treatment of mixes. M.V.K.

PATENTS

Arcing guide for insulators. A. O. AUSTIN (Ohio Brass Co.). U. S. 1,972,613, Sept. 4, 1934.

Closet. H. E. HARTWELL. U. S. 1,972,774, Sept. 4, 1934.

Closet bowl and tank structure. C. H. ZWERMANN. U. S. 1,970,789, Aug. 21, 1934.

Flush tank and closet-bowl combination. G. P. GAVIN AND F. G. BROTZ. U. S. 1,970,799, Aug. 21, 1934.

Flushing tank. WILLIAM TAYLOR (James M. Teahan). U. S. 1,971,880, Aug. 28, 1934.

Insulator. A. O. AUSTIN (Ohio Brass Co.). U. S. 1,972,614, Sept. 4, 1934.

Lavatory. C. H. ZWERMANN. U. S. 1,970,790, Aug. 21, 1934.

Lavatory support. C. H. ZWERMANN. U. S. 1,970,791, Aug. 21, 1934.

Means for controlling the electrostatic field for insulator bushings. RALPH HIGGINS (Ohio Brass Co.). U. S. 1,972,590, Sept. 4, 1934.

Strain insulator. A. O. AUSTIN (Ohio Brass Co.). U. S. 1,972,615, Sept. 4, 1934.

Equipment and Apparatus

Air conditioning in industry. Review of possible developments. M. C. MARSH. *Chem. & Ind.*, **53** [31], 671–79 (1934).—M. discusses (1) measurement of humidity, (2) automatic humidity control, and (3) methods of increasing and decreasing humidity. G.R.S.

Brightness meter for luminous preparations. L. F. CURTISS. *Jour. Research Nat. Bur. Stand.*, **13** [2], 203–205 (1934); R. P. 702, price 5¢. R.A.H.

Checking accuracy of cement-testing sieves. ANON. *Cement & Cement Manuf.*, **7** [8], 258–59 (1934).—An image of the wire mesh magnified 100 times is projected on a ground-glass screen. The apertures and the wires in the projected image are measured with screw dividers and an ordinary scale. G.R.S.

Corrosion-resisting material for the chemical industry. ANON. *Werkstoffe & Corrosion*, **9** [7], 26 (1934).—A new alloy, Corrix Metal, consists of 88.1 Cu, 8.7 Al, and 3.05% Fe, and has in cast state a tensile strength of 55 to 65 kg./mm.^{2} at an elongation of 20 to 30%; it can be rolled, pressed, forged, drawn, hardened, and welded and has a fine grain structure. Corrosion resistance is superior to austenitic Cr-Ni steels. HCl, 50% acetic acid, thiosulfate, and ammonium chloride attack it in the beginning, but this soon ceases and a state of equilibrium is formed. It resists almost all organic and inorganic acids and lyes. It is used in chemical plants where it comes in contact with ammonia. A list of chemicals and loss of weight when exposed to them is added. M.H.

Criteria for industrial exhaust systems. J. J. BLOOMFIELD. *Heating, Piping & Air Conditioning*, **6** [7], 319–24 (1934).—B. considers the methods and instruments used in testing the efficiency of industrial exhaust systems for removing toxic dusts, fumes, gases, and vapors. Under sampling and analysis of dusts, he discusses fibrosis-producing dusts, composition of industrial dusts, size of dusts, quantity of dust, and poisonous dusts. Methods for collecting and testing of fumes, gases, and vapors are discussed. The application of the test methods described is outlined. Bibliography. See also *Ceram. Abs.*, **12** [10–11], 406 (1933). J.L.G.

De-airing process for sewer-pipe and conduit manufacture. ROBERT C. ZEHM. *Bull. Amer. Ceram. Soc.*, **13** [9], 224–26 (1934).

Derivation of photometric standards for tungsten-filament lamps. H. T. WENSEL, WM. F. ROESER, L. E. BARBROW, AND F. R. CALDWELL. *Jour. Research Nat. Bur. Stand.*, **13** [2], 161–68 (1934); R. P. 699, price 5¢.—A method for comparing the candlepower of carbon and tungsten lamps is described which avoids the usual difficulties of heterochromatic photometry. An empirical formula is given for the brightness of a black body over the range 1550 to 2727°K. R.A.H.

Dies for automatic presses in ceramics. LOUIS SACKLOVSKI. *Sprechsaal*, **67** [23], 341–43; [24], 358–60; [25], 373–75; [26], 385–86 (1934).—Illustrated. M.V.K.

Drying with reference to the use of waste heat. A. BIANCHI. *Calore*, **4**, 73–77 (1932); abstracted in *Bibliografia Italiana*, **5** [9–10], 101 (1932).—B. discusses the problem of drying and considers particular examples of drying installations in Italy. H.F.V.

Electric control of furnace temperature. A. M. TOUVY. *Rev. mat. constr. trav. pub.*, No. 296, pp. 85–88*B* (1934).—The use of electric pyrometers and photoelectric cells for measuring furnace temperatures is discussed. Various types are briefly described. M.V.K.

Electric furnace for determining fusion temperature of coal ash. A. DAWE AND C. W. FALKNER. *Fuel Sci. Practice*, **13** [8], 230–36 (1934).—The furnace consists of an inner one-inch tube wound with a platinum-rhodium alloy wire which is preheated by means of a tube of a larger diameter wound with a nickel-chromium wire. These parts can be removed easily and independently for renewal when necessary. A saturator is attached for providing a reducing atmosphere of 50% hydrogen-50% water-vapor. The method of carrying out a determination, including the preparation of test cones, is described. Results are given of tests on the effect of the shape and size of the test piece. Cones, threads, and small cylinders give almost identical results. A thermocouple is used for temperature measurement. Illustrated. F.G.H.

Electric temperature and humidity control in wood and drying chambers. G. H. ZIRKER. *Giesserei*, **21** [31–32], 327–32 (1934).—Z. describes principles of electric measurements of temperature and humidity and arrangement of drying chambers for wood, foundries, and ceramic plants. M.H.

Electrophoresis as applied to chemical stoneware. J. M. W. CHAMBERLAIN. *Ind. Eng. Chem., News Ed.*, **12** [16], 303 (1934).—The basic problems involved in the electrophoretic extrusion of clay bodies from dies are briefly discussed. Proper design and insulation of dies and the balancing of raw clay mixtures to obtain proper results are important. F.G.H.

Fan for forced and induced draft. A. A. CRIQUI. *Power*, **78** [5], 250–51 (1934).—Performance characteristics of straight, forward-curved, and double-curved blades are discussed with reference to their suitability for use as forced- or induced-draft fans. Illustrated with curves. F.G.H.

Magnifying glass with self-illuminating field of vision. G. JAECKEL. *Z. tech. Physik*, **14** [11], 499–500 (1933).—The principle underlying this magnifying glass is the combination of a hemisphere with a cylindrical part. Beams of light passing between the object studied and the head

of the observer will be concentrated and will illuminate the field of vision. W.M.C.

Measuring gloss and texture of surfaces. I. RICHARD S. HUNTER. *Amer. Enameler*, **7** [4], 3–4 (1934).—H. describes the Glossmeter and the method of gloss reading. **II.** *Ibid.*, **7** [5], 7–8 (1934).—The method of surface examination and theory of the gloss scale are given. H.T.

Measuring reflective and transmissive properties of diffusing media. H. J. MCNICHOLAS. *Jour. Research Nat. Bur. Stand.*, **13** [2], 211–36 (1934); R.P. 704, price 5¢.—The construction and operation of equipment is described for studies of the diffusion and absorption of light by materials such as textiles, papers, paints, enamels, etc., for which measurements of color, gloss, transparency or optical density, hiding and tinting powers, or similar properties are required. R.A.H.

Mill casings: chilled cast iron or cast steel? E. POLLACK. *Tonind.-Ztg.*, **58** [46], 550–51 (1934). M.V.K.

Moving the work and the worker. WALTER H. EMERSON. *Ceram. Ind.*, **23** [3], 138–43 (1934).—The unique new bisque placing conveyer at the Homer Laughlin China Co., on which the work as well as the workman are moved, economizes on saggers, speeds up operations, and saves the workmen's energy. A detailed description of the 750-ft. U-shaped conveyer is given. Illustrated. E.J.V.

Power and heat in coarse ceramics. W. LEDER. *Ziegelwelt*, **64** [5], 47–48; [6], 58–59; [7], 68–69 (1934).—L. discusses the economical consumption of heat by various furnaces. See also *Ceram. Abs.*, **12** [3], 107 (1933). M.V.K.

Psychrometric chart. E. COWAN. *Power*, **78** [3], 140 (1934).—Several scales are included on *Power's* data sheet No. 19. F.G.H.

Testing clay for greater efficiency in drying practice. ERNEST W. KNAPP. *Brick Clay Rec.*, **85** [2], 57–60 (1934).—In making drying tests on clays, a proved clay shape should be used to establish facts regarding drying characteristics of the raw material. During tests of wet-bulb, dry-bulb, and clay temperatures, the shrinkage progression, notes on observations, fan speeds, behavior of ware, etc., should be kept. The clay temperature should be maintained slightly above the wet-bulb temperature. After shrinkage is complete the dry-bulb temperature may be raised to the maximum for comparative results, and the drying operation is maintained until the clay temperature is equal to the dry-bulb temperature, when the piece is considered commercially dry. Results of tests showing the effect of varying conditions are given. Experience with high humidity conditions is discussed. Illustrated. See also *Ceram. Abs.*, **13** [9], 239 (1934). E.J.V.

Testing instruments for measuring moisture content of gases containing dust. K. GUTHMANN. *Arch. Eisenhüttenwesen*, **7**, 673–78 (1934).—Instruments tested included mercury thermometers and instruments recording over long distances. Best results were obtained with an instrument by Siemens and Halske which proved to be of high sensitivity and great accuracy. Both relative and absolute humidities are recorded by this instrument. W.M.C.

Torsion thermometer with stepped springs. A. KARSTEN. *Z. Instrumentenk.*, **54** [8], 274–77 (1934).—Instruments up to 440°C have been built which successfully replace liquid thermometers. M.H.

Transmission by gearing and motors with reducers applied to ceramic machines. I. PIERRE RENAULT. *Rev. mat. constr. trav. pub.*, No. 295, pp. 70–74*B*; No. 296, pp. 92–94*B*; No. 297, pp. 111–13*B*; No. 298, pp. 130–34*B* (1934).—Illustrated. M.V.K.

Viscosity of petroleum products. Methods and apparatus for viscosity measurement. E. A. WILLIHNGANZ, W. B. MCCLUER, M. R. FENSKE, AND R. V. MCGREW. *Ind. Eng. Chem., Anal. Ed.*, **6** [4], 231–34 (1934).—Illustrated. F.G.H.

BOOK AND BULLETINS

Driving Rates and Power Performance in Jaw Crushers, Especially in Large Crushers (Antriebsverhältnisse und Kräftespiel an Backen-Steinbrechern, Insbesondere, an Grossbrechern). A. BONWETSCH. V.D.I. Verlag, Berlin, 1933. 41 pp. Price 10.75 Rm. Reviewed in *Mech. Eng.*, **56** [2], 124 (1934).—This report covers an exhaustive study of jaw crushers, especially those of large size, undertaken to throw light upon the stresses during operation, power requirements, etc. F.G.H.

Indicating Pyrometer. ANON. *Foxboro Co. Bull.*, No. 192; reviewed in *Foundry*, **62** [4], 77 (1934).—The potentiometer type of indicating pyrometer is described. The temperature scale on the unit is drawn on a dial 6 in. in diameter and provides 17 in. of actual temperature scale; it can be read with great precision. Illustrated. F.G.H.

Mixing Machines. LANCASTER IRON WORKS. 36 pp. Reviewed in *Foundry*, **62** [3], 70 (1934).—Various mixing machines for the abrasive, ceramic, chemical, cement, and glass fields are described. The mixers have a slowly rotating pan moving counter to one or two rapidly rotating mixing stars. F.G.H.

PATENTS

Batch-weighing apparatus. W. C. BATES AND J. O. KROSSE (Standard Silicate Co.). U. S. 1,971,807, Aug. 28, 1934.

Clay-firing furnace. JULIUS HANSEN (Shell Petroleum Corp.). U. S. 1,969,979, Aug. 14, 1934.

Drying floor for china clay. R. J. VARCOE. U. S. 1,972,670, Sept. 4, 1934. A drying floor for china clay, etc., comprises hard, heat-insulating material in which are embedded heating pipes having substantially flat, exposed upper portions, the portions of the floor between the exposed upper portions of the pipes being overlaid with a relatively thin firm layer of china clay leaving a smooth upper surface substantially flush with the exposed upper portions of the pipe.

Metallographic polishing machine. J. P. BUCKLEY. U. S. 1,972,086, Sept. 4, 1934.

Kilns, Furnaces, Fuels, and Combustion

Analysis of gaseous hydrocarbons. Determining gaseous paraffins and olefins. H. TROPSCH AND W. J. MATTOX. *Ind. Eng. Chem., Anal. Ed.*, **6** [4], 235–41 (1934). F.G.H.

Burning characteristics of pulverized coals and radiation from their flames. R. A. SHERMAN. *Combustion*, **5** [12], 30–38 (1933); abstracted in *Fuel Sci. Practice*, **13** [5], 159 (1934).—An investigation of the combustion of pulverized fuels in a large-scale laboratory apparatus is described. The object was to determine the relation of the rate of burning of pulverized fuels and of the radiation from their flames to the type of fuel and the fineness of pulverization. The results are stated, the data on the radiation from the flames being presented in curves. Diagrams illustrate the furnace and burner used and the apparatus for measurement of radiation. It is shown that (1) fineness of grinding becomes exceedingly important as the combustion space is restricted, (2) the type of coal influences the rate of combustion, and (3) although the temperature and total radiation of the flame are affected by fineness of grinding, excess aid, and rate of firing, the emissivity of the flame at any position of the burner is affected only by the type of coal. F.G.H.

Burning pulverized lignite. R. F. THRONE. *Mech. Eng.*, **56** [6], 325–29 (1934).—Operating experiences in the burning of Colorado lignite in refractory and slag-tap furnaces are described and discussed. Illustrated. F.G.H.

Characteristics of a coalification series. H. A. J. PIETERS, H. KOOPMANS, AND J. W. T. HOVERS. *Fuel Sci. Practice*, **13** [3], 82–86 (1934).—The plasticity range during the carbonization of coal, oxidation curves of coal, and the relative ignition temperatures of a coalification series are described. Illustrated. F.G.H.

Combustion rate of carbon. I. Combustion of spheres in flowing gas streams. C. M. TU, H. DAVIS, AND H. C. HOTTEL. *Ind. Eng. Chem.*, **26** [7], 749–57 (1934).—Data are presented on the rate of combustion of spheres of carbon in various nitrogen-oxygen mixtures, under conditions in which both the rate of chemical reaction at the surface and the rate of diffusion of oxygen to the surface are factors. A quantitative formulation of combustion rate is presented, predicting effects of temperature, gas velocity, and gas composition in agreement with the experimental measurements. The combustion-rate equation is able to establish limits within which the absolute magnitude of the combustion rate must lie, but these limits are rather broad because of the lack of data on gas diffusivities at high temperatures and of an inexact knowledge of the net products of the primary reaction between oxygen and carbon. From similar data for the rate of combustion in carbon dioxide it is concluded that carbon, when burned in air, is consumed by direct oxidation with oxygen rather than by a mechanism in which oxygen is pictured as reaching the surface chiefly in the form of carbon dioxide, there forming carbon monoxide. Illustrated with curves and diagrams. **II. Combustion at a surface overlaid with stagnant gas.** H. DAVIS AND H. C. HOTTEL. *Ibid.*, **26** [8], 889–92 (1934).—Data have been obtained for the rate of combustion of several types of carbon in cups of varying depths and compared with a quantitative formulation of combustion rate under conditions in which diffusion controls the rate. The experimental results are found to lie within the limits imposed by the theory. The rate of combustion, for a given distance of diffusion of oxygen to the carbon surface, decreases with an increase in the degree of graphitization of the carbon. This is interpreted as indicating a decrease in the ratio of carbon monoxide to carbon dioxide formed as primary products of combustion at the carbon surface. Photographic studies of the combustion of spheres indicate the existence of a zone about the spheres in which counter-diffusing oxygen and carbon monoxide burn. Illustrated. F.G.H.

Continuous determination and recording of carbon dioxide content of gas mixtures. A. S. SMITH. *Ind. Eng. Chem., Anal. Ed.*, **6** [4], 293–95 (1934).—A modification of the method described by White, which improves its operation and adaptability in plant installation, is briefly described. The apparatus, as modified, has given satisfactory service in a plant installation for recording concentrations of carbon dioxide from 0.1 to 1.0% in natural gas. Illustrated. F.G.H.

Determining rate of evolution of gas from coal. D. J. W. KREULEN. *Fuel Sci. Practice*, **13** [6], 190–91 (1934).—Illustrated. F.G.H.

Economy in fuel by preheating air. JAESCHKE. *Emaillwaren-Ind.*, **11** [29], 241–42 (1934).—Formulas are developed showing theoretical economies. Data from practice are given. M.V.K.

Electric resistance furnaces in industry. ANON. *Jour. four élec.*, **43** [8], 232–90 (1934).—Descriptions, with diagrams and photographs, of a large number of electric furnaces used in industry are given. G.R.S.

Equilibrium concentrations of gases in flames. H. SEAMAN AND B. LEWIS. *Fuel Sci. Practice*, **13** [3], 87–91 (1934). F.G.H.

Firing grog products with anthracite. N. A. MIGULIN. *Ogneuporui*. No. 9 (1933); abstracted in *Keram. i Steklo*, **10** [6], 38 (1934).—Experiments showed that anthracite is suitable for firing grog products. Lack of smoke and a complete combustion reduces to a minimum the losses due to chemically incomplete combustion. M.V.K.

Firing refractories and their stability. VEY. *Rev. mat. constr. trav. pub.*, No. 295, pp. 76–77*B* (1934).—The firing of refractories and the properties of brick for furnace crowns are discussed. The best firing is obtained in special continuous blast furnaces with a direct or reversed flame and in blast tunnel kilns with a direct flame. M.V.K.

Firing vitrifiable inscription on glass and ceramic ware. L. DUBUIT. *Verre & Silicates Ind.*, **5** [12], 228–29 (1934).—Directions are given for firing glass or ceramic ware with various types of inscriptions. A muffle kiln with an oxidizing atmosphere is used. M.V.K.

Gas- and flame-temperature measurement. A. v. ENGEL AND M. STEENBECK. *Arch. tech. Mess.*, **3** [9], 115–16 (1933); abstracted in *Fuel Sci. Practice*, **13** [6], 191 (1934).—The determination of gas temperature by direct thermometric methods, gas-density measurements, and radiation methods is discussed. Bibliography. F.G.H.

Gas generator. A. JAESCHKE. *Glashütte*, **64** [18], 287–89 (1934).—A brief review of various present-day devices used to increase the efficiency of gas generators is given. M.V.K.

Graphical method of calculating pure coal calorific value. G. THIESSEN AND F. H. REED. *Fuel Sci. Practice*, **13** [6], 167–75; [7], 208–17 (1934).—Formula methods, as illustrated by the Parr unit coal formula, and graphical methods, making use of analyses of float-and-sink fractions of coal samples, are used for finding pure coal values. If the mineral matter absorbs or evolves considerable heat in transformation, the graphical method will not give the correct value unless the intercept of the curve with the ordinate representing the calorific value of the mineral matter is taken. The actual variations from a straight-line relationship resulting from the causes suggested are small, and the values obtained by the graphical method closely approach accuracy and provide a satisfactory means of testing the adequacy of empirical formulas, such as the Parr formula, for arriving at a value for mineral-free coal. Since Parr unit coal calorific values can be calculated from published proximate coal analyses and special procedures of analyses are not required, Parr's formula method has much wider application than the graphical method. Illustrated. F.G.H.

Heat flow through granulated material. T. E. W. SCHUMANN AND V. VOSS. *Fuel Sci. Practice*, **13** [8], 249–56 (1934).—An approximate formula is developed which gives the thermal conductivity of a heterogeneous system, consisting of a continuous phase and a disperse phase, in terms of the conductivities of the two constituents and their respective concentrations. Though the formula is only approximate, experiments show that it is of wide validity when great accuracy is not insisted upon. The theory accounts well for the observed phenomena, and results may lead to important practical applications. Illustrated. F.G.H.

Heavy oil burners. R. D. *Verre & Silicates Ind.*, **5** [13], 242–44 (1934).—Types of burners are described. Illustrated. M.V.K.

High-hydrogen water gas from younger coal cokes. R. E. BREWER AND L. H. REYERSON. *Ind. Eng. Chem.*, **26** [7], 734–40 (1934). F.G.H.

Hints for rapid firing. ANON. *Brit. Clayworker*, **43** [507], 113; [508], 145–46 (1934).—Seventeen suggestions are given for fuel control, draft, setting of ware, etc., that will speed up firing and increase the output of tunnel kilns. R.A.H.

Mathematical valuation of waste-gas analyses taking into consideration a variation of the oxygen content of the air for combustion. A. R. LEYE. *Feuerungstechnik*, **22** [5], 53–56 (1934). M.V.K.

Method for measuring the rate of high-velocity gas reactions. L. FROMMER AND M. POLANYI. *Trans. Faraday Soc.*, **30** [7], 519–29 (1934).—The reaction rate, k, of a bimolecular gas reaction can be measured in the following way: A known stream, n, of particles of a gas, A, is introduced into a reaction chamber containing an excess concentration, c, of the other reacting gas, B, and the number, N, of particles of A in the stationary reaction zone ("flame") is measured, obtaining $K = n/N \cdot c$. The results are in agreement with measurements of the reaction rate made by the "diffusion method" in its revised form. The method is free from any of those assumptions as to the special distribution of the gas A in the "flame" which are essential to the diffusion method. This method seems also to extend over a wider range of velocities and reacting substances than the diffusion method. G.R.S.

Microanalytical determination of carbon and hydrogen. J. B. NIEDERL AND R. T. ROTH. *Ind. Eng. Chem., Anal. Ed.*, **6** [4], 272–74 (1934).—A simplified method, much improved, for the microdetermination of carbon and hydrogen is described and discussed. Illustrated. F.G.H.

Practice of firing brick. HERM. MAGER. *Tonind.-Ztg.*, **58** [52], 624–25; [53], 639–40 (1934).—Factors influencing firing include (1) characteristics of the furnace, (2) charging, (3) amount of air of combustion, and (4) fuel, etc. M.V.K.

Recent developments in coal utilization. A. C. FIELDNER. *Fuel Sci. Practice*, **13** [5], 131–37 (1934). F.G.H.

Rotary electric kiln. ANON. *Mech. World*, **96** [2487], 193 (1934).—The special features of Rotolec, a kiln consisting of a circular chamber within which a circular table revolves, are enumerated. Illustrated. E.J.V.

Stoneware and vitrified tile furnaces. JOSEPH GREWE. *Tonind.-Ztg.*, **58** [49], 589–91; [50], 602–603 (1934).—Construction defects of various types of furnaces for firing stoneware and vitrified tile are discussed. M.V.K.

BOOKS AND BULLETINS

Collected Papers on the Knowledge of Coal (Gesammelte Abhandlungen zur Kenntnis der Kohle). **Vol. XI, 1931 to 1933.** Kaiser Wilhelm Coal Research Institute, Mulheim-Ruhr, Germany. 708 pp. Price 74 Rm, 50 pfg. Reviewed in *Fuel Sci. Practice*, **13** [7], 226 (1934). F.G.H.

Combustion. 3rd ed. G. SEGELER. American Gas Association, New York, 1933. 208 pp. Price $2.00. Reviewed in *Power*, **78** [5], 267 (1934). F.G.H.

Gas Engineers' Handbook. PACIFIC COAST GAS ASSOCIATION. McGraw-Hill Book Co., Inc., New York, 1934. 1017 pp. Price $7.50. Reviewed in *Ind. Eng. Chem., News Ed.*, **12** [15], 284 (1934). F.G.H.

Gas Generator in the Ceramic Industry (Gazogenerator v keramicheskoi promuishlennosti). D. B. GINZBURG. Gostroiizdat, 1933. 189 pp., 76 illustrations. Reviewed in *Keram. i Steklo*, **10** [7], 39–40 (1934).—After a review of fuel properties and basic principles of gasification, a detailed discussion is given of the construction of gas generators, gas pipes and valves, conveyance of air and steam, drying and purifying gas, control and operation of gas generators, and thermal balance. M.V.K.

Mathematical Consideration of the Combustion Processes and Waste Gases in Furnaces, Especially in Lime and Cement Kilns (Rechnerische Betrachtungen über Verbrennungsvorgänge und Abgasverluste bei Feuerungen, insbesondere bei Kalk- und Zementöfen). Z. KERTESZ. Wilhelm Knapp, Halle (Saale), Germany, 1934. 72 pp. Price 4.80 Rm; bound 6.00 Rm. Reviewed in *Jour. Amer. Chem. Soc.*, **56** [4], 1004 (1934). F.G.H.

Underfeed combustion, effect of preheat, and distribution of ash in fuel beds. P. NICHOLLS. *Bur. Mines Bull.*, No. 378, 76 pp. (1934); price 10¢ from Supt. of Documents, Washington, D. C.—Results of an investigation on the burning of solid fuels to measure reaction in the fuel beds in the burning of the fuel and in the clinkering of its ash are reported. Studies of the underfeed type fuel bed, exemplified by underfeed stokers, and the effect of preheated air on what transpires in both overfeed and underfeed fuel beds are given. R.A.H.

PATENTS

Car propeller for kiln, etc. BRITISH CERAMIC SERVICE CO., LTD., AND C. A. HOFFMAN. Brit. 414,071, Aug. 9, 1934.

Electric muffle furnace. O. JUNKER GES. Brit. 414,643, Aug. 22, 1934.

Fuel burner. W. H. BYRNE AND C. H. BYERS. U. S. 1,971,328, Aug. 28, 1934.

Tunnel kiln. S. M. KIER AND F. M. HARTFORD. U. S. 1,970,320, Aug. 14, 1934.

Tunnel kiln. T. W. SHOOK. Brit. 414,610, Aug. 15, 1934.

Manufacture of barium fluosilicate and its applications. GRASSELLI CHEMICAL CO. Brit. 414,110, Aug. 9, 1934.

Process of treating alunite. H. G. WILDMAN (Carl H. Fowler). U. S. 1,971,319, Aug. 21, 1934. A wet process of treating alunite for recovery of alumina and potash comprises grinding the alunite, treating with an excess of caustic potash solution until dissolved, filtering the solution to remove any undissolved residue, precipitating aluminum hydroxide from the filtrate by treating with carbon dioxide, filtering out the aluminum hydroxide from the solution, evaporating the filtrate to crystallize out potassium sulfate, filtering the solution to remove potassium sulfate, and then treating the filtrate with lime to recover the caustic potash.

Geology

Detection of zeolitic nature of trass. K. BIEHL AND W. WITTELKIND. *Tonind.-Ztg.*, **58** [41–42], 499–501; [43], 515–16 (1934).—It was determined that trass consists partly of zeolites. The analysis method developed can be used for natural zeolites. Details are given. M.V.K.

Dust-like silica of Magnitorsk. I. I. KITAIGORODSKII. *Keram. i Steklo*, **10** [6], 30–31 (1934).—From the mineralogical viewpoint, the Magnitorsk dust-like silica represents a thin powder consisting of quartz grains of 0.005 to 0.05 mm. The sand contains many needle-like prismatic crystals. The chemical analysis is 95.62 SiO_2, 3.91 Al_2O_3, 0.17 Fe_2O_3, 0.35 MgO, and 0.15% CaO. This dust-like sand can be easily enriched chemically. M.V.K.

Lepidolite deposits "Rozna" in Moravia as lithium ore deposits. H. MOHR. *Berg- und Hüttenmännisches Jahrbuch*, **82** [2], 44–50 (1934).—The deposits of lepidolite are of great extent and form one of the earth's few important sources of Li. Its composition is usually $F_2KLiAl_2Si_3O_9$, with a Li content of 4.1%. The particular advantages of this mineral, in most cases occurring as pure pink colored mica, are its relative frequent occurrence and easy working with H_2SO_4; it also contains some Ru, Cs, and Th. Li and its salts have found wide application. The Al alloy, Scleron, contains 0.1% Li; the bearing metal of the German state railways consists of 0.69 Ca, 0.62 Na, 0.04% Li, small amounts of Al, and the remainder Pb. Li is used as deoxidizer for Cu, Ni, etc., and as addition to solders for Al. The ceramic industry uses lepidolite or Li minerals for producing milk-white glasses and for glazes which must resist chemical attack or sudden temperature changes. Present yearly production of Li metal amounts to several thousand kg.; the price is about 165 to 175 M. per kg. Geological conditions and mining possibilities are described. Bibliography. M.H.

Lithium. FREITAG. *Emailwaren-Ind.*, **11** [30], 249–50 (1934).—The production of metal lithium and its use and properties are briefly discussed. M.V.K.

Organic siliceous powders or kieselguhr. V. C. *Verre & Silicates Ind.*, **5** [14], 262–64 (1934).—A brief discussion of the origin, properties, and application of kieselguhr in industry is given. M.V.K.

Production of pulverized flint (quartz). H. F. SPIER. *Amer. Enameler*, **7** [5], 5 (1934).—A short history of materials is given. Location and mining methods used in producing quartz are described. H.T.

Relations between original structure of the disperse phase of original soils and the crystalline and metasomatic transformation of sediments. J. P. AREND. *Compt. rend.*, **199** [2], 155–57 (1934).—Studies of ferruginous minerals showed that calcareous oölite could never have been formed beside a ferruginous oölite. M.H.

Talc industry in the Piedmont. L. PARLATI. *L'Industria* [Milan], **5**, 137–38 (1932); abstracted in *Bibliografia Italiana*, **6** [1–2], 3 (1933).—A short note on the progress of the talc industry is given. H.F.V.

BOOK

Fluorspar: Occurrences, Mining, Working, and Economic Significance (Der Flussspat: Vorkommen, Gewinnung, Verarbeitung und wirtschaftliche Bedeutung). F. MEDENBACH. Mineralogical Soc., Weilburg. 248 pp., 30 illustrations. Bound, 8.00 Rm. Reviewed in *Tonind.-Ztg.*, **58** [46], 556 (1934). M.V.K.

Chemistry and Physics

Analysis of calcium carbonate. PEMCO LABORATORIES. *Amer. Enameler*, **7** [4], 6 (1934).—The prescribed method for the analysis of calcium carbonate in determining its suitability for high-grade porcelain enamels is given. H.T.

Analysis of clays and other ceramic raw materials. ALIX CORNILLE. *Rev. mat. constr. trav. pub.*, No. 295, pp. 61–67*B* (1934).—Details are given of various methods used for determining the alumina content, including (1) sodium carbonate method, (2) hydrofluoric method, (3) calcium carbonate method, (4) treating with sulfuric acid, (5) baryta method, and (6) calcining and treating with

hydrochloric acid. The advantages of the methods are discussed. M.V.K.

Base-exchange reactions of bentonite and salts of organic bases. C. R. SMITH. *Jour. Amer. Chem. Soc.*, **56** [7], 1561–63 (1934).—The reaction between bentonite and salts of organic bases is principally one of base exchange. Bentonite enters into base exchange with a definite chemical equivalent of organic bases where saturation can be reached. In the one sample of bentonite used 1 g. combined with 6.2 to 6.4 cc. of 0.1 *N* organic base. When saturation is approached with most bases flocculation is produced. Flocculation indicates that a reaction has taken place with partial or complete saturation of the silicate. Saturation is promoted by the insolubility of the silicate complex and by the removal of the inorganic salts by washing. F.G.H.

Colloidal nature and related properties of clays. W. W. MEYER. *Jour. Research Nat. Bur. Stand.*, **13** [2], 245–58 (1934); R.P. 706, price 5¢.—A theory on the colloidal nature and related properties of clays is presented, based upon the findings of soil scientists and the existing knowledge of the phenomena of coagulation, deflocculation, plasticity, drying shrinkage, and dry transverse strength. Clay particles are formed by the partial or complete combination of weak acids and weak bases, the ratio of the combination depending upon the p_H value of the weathering solution. Basic and acidic residues occur at the particle surfaces and can dissociate to form an ion atmosphere, leaving ionic charges on the particles. The degree of ionization of these adsorbed atoms and groups is controlled by the concentration of like ions in the intermicellar solutions. The ratio of acidic to basic residue of the particle depends upon the composition of the surface layer. The nature and number of the micellar ions influence various properties of the clay. The clay tends to weather to the composition which has an isoelectric p_H value of the weathering solution. For this reason the more completely a clay is weathered by a given solution, the less fine particles it will contain because it reaches the isoelectric composition. In this condition there is a minimum density of the micellar ion atmosphere and maximum particle growth resulting from combination of the acidic and basic residues of adjacent particles. A low ratio of acidic to amphoteric constituents also corresponds with a low micellar ion density. The colloidal properties of a clay are due to the presence of the ionic atmosphere mentioned above. The maximum size of particles which can exhibit colloidal properties depends upon the activity of their surface layers, which in turn depends upon their compositions. An increase in the ratio of acidic to amphoteric constituents or substitution of iron for aluminum or humic acid for silicic acid decreases the activity. Osmotic imbibition of water which depends upon the micellar ion atmosphere accounts in a large measure for the colloidal properties of clays. The base-exchange capacity, at a specified p_H value, is indicative of a clay's capacity for imbibed water, under given conditions. The determination of the properties of clays as outlined in this paper would not only furnish a means of classification, but would yield information which could be applied to the problem of clay beneficiation. R.A.H.

Colorimetric determination of traces of fluorine. L. SZEGOE AND B. CASSONI. *Giorn. chim. ind. applicata*, **15** [12], 599–602 (1934).—Minute quantities of F can be detected by a method based on the distillation of silicon tetrafluoride or fluosilicic acid and colorimetric measurement of F in the distillate by the Pulfrich photometer. SiF_4 does not give satisfactory results, however, if large quantities of colloidal Si are present; in this case, fluosilicic acid should be used. Illustrated by example. M.H.

Crystal structure of ammonium beryllium fluoride $(NH_4)_2BeF_4$. R. HULTGREN. *Z. Krist.*, **88** [3], 233–37 (1934).—The orthorhombic crystal $(NH_4)_2BeF_4$ was investigated with the following results: $a_0 = 5.8$Å, $b_0 = 10.27$Å, and $c_0 = 7.5$Å. The atomic arrangement is that of K_2SO_4; this structure is also assumed by $(NH_4)_2SO_4$. This shows that the BeF_4^{2-} group has almost the same size and shape as the SO_4^{2-} group, which is to be expected from consideration of ionic sizes. G.R.S.

Crystal structure of ilmenite. T. F. W. BARTH AND E. POSNJAK. *Z. Krist.*, **88** [4], 265–70 (1934).—From powder oscillation and Weissenberg X-ray photographs of ilmenite, its atomic arrangement, which is controlled by five parameter values, was completely determined. In accordance with the observed external symmetry of ilmenite it was found that crystals of the mineral are isomorphous with the space group C_{3i}^2, which is a subgroup of the space group of corundum, D_{3d}^6. The structure of ilmenite is so closely related to that of corundum that it seems appropriate to regard these structures as belonging to the same type, the corundum-ilmenite type. G.R.S.

Determination of Al_2O_3 and Fe_2O_3 in clay. K. ZIMMERMANN. *Chem. Weekblad*, **31** [19], 317–19 (1934).—In analyzing clay, Al_2O_3 and Fe_2O_3 are simultaneously precipitated by NH_4OH. Since dehydration of Al_2O_3 is fairly difficult and calcined Al_2O_3 absorbs water very slowly, Al_2O_3 is best calcined at a high temperature. Calcining at high temperature transforms Fe_2O_3 into Fe_3O_4 by giving up O_2. Tests were made to determine the best temperature for calcining mixtures containing $Al_2O_3 + Fe_2O_3$. It was found that at 1300°C Al_2O_3 is practically water free and even at 1200° good values were obtained. The higher the Al_2O_3, and the lower the Fe_2O_3 contents of a mixture, the higher should be the calcining temperature. The best temperature should be determined from case to case. A few examples on how to proceed are described. M.H.

Determination of small quantities of sodium carbonate. Warder's method with improved technique. J. E. S. HAN. *Ind. Eng. Chem., Anal. Ed.*, **6** [3], 209 (1934).—Improvements for carrying out the double-indicator titration are suggested. F.G.H.

Determination of total carbon in soils by wet oxidation method. J. E. ADAMS. *Ind. Eng. Chem., Anal. Ed.*, **6** [4], 277–79 (1934). F.G.H.

Determination of zinc in the presence of uranium. W. R. WIGGINS AND C. E. WOOD. *Jour. Soc. Chem. Ind.*, **53** [32], 254 (1934).—Two methods are given to prevent precipitation of uranium as the 8-hydroxyquinoline salt and give accurate results in the determination of zinc. G.R.S.

Equilibrium diagram of cobalt-silicon. R. VOGEL

AND K. ROSENTHAL. *Arch. Eisenhüttenwesen*, **7**, 689–91 (1934).—A new compound, Co_2Si, shows up in the melt at 1210°C and decomposes at 1160°. A transformation point occurs at 1332°. Both modifications form mixed crystals with an excess of silicon; the β-mixed crystal with 20.8% Si decomposes at 1208° into an α-mixed crystal with 19.8% Si and into the compound CoSi. No compound was found of the formula Co_3Si_2.

W.M.C.

Equilibrium diagram of the system Na_2TiO_3–K_2TiO_3. U. NISIOKA. *Sci. Repts. Tôhoku Imp. Univ.*, **23** [2], 259–64 (1934).—Samples were prepared by melting, in an electric resistance furnace, a mixture of titanium dioxide, potassium carbonate, and sodium carbonate. The equilibrium diagram was derived from thermal analyses. This system shows a eutectic point at 773°C with 18 mol. % of Na_2TiO_3 and a monotectic point at 893° with a range from 50 to 80 mol. % of Na_2TiO_3. W.M.C.

Microanalysis of gaseous mixtures by pressure-temperature curves. J. J. S. SEBASTIAN AND H. C. HOWARD. *Ind. Eng. Chem., Anal. Ed.*, **6** [3], 172–77 (1934).—An apparatus and procedure has been developed whereby an accurate analysis of less than 1 milliliter of gas can be made in 3 to 5 hr. The sample is not destroyed and may be analyzed again. The method has been applied successfully to the analysis of synthetic mixtures of pure hydrocarbons, commercial gas samples, and gaseous products obtained in the thermal decomposition of coal. Where two components form a heterogeneous condensed phase, the determination is simple; if they form a homogeneous condensed phase and have normal boiling points lying close to each other, the determination is more difficult but still possible. A limitation of the method as developed at the present time lies in the impossibility of determining saturated and unsaturated hydrocarbon gases of the same number of carbon atoms in a mixture. Methods of obviating this difficulty are given. The method depends on a temperature difference between the evaporation bulb and the remainder of the system, and hence can be applied to higher boiling mixtures if suitable pressure-measuring and temperature-control devices are used. Illustrated. F.G.H.

Oriented inclusion of impurities in crystals. H. E. BUCKLEY. *Z. Krist.*, **88** [3], 248–55 (1934).—Impurity may adhere and become included in crystals on certain planes, whose growth rates are at the same time modified. Other methods of inclusion are described. It is shown that adhesion of impurity and modification of crystal-habit may be independent of each other. G.R.S.

Oxidation of iron in slag depending on chemical composition, temperature, and furnace atmosphere. H. SALMANG AND J. KALTENBACH. *Arch. Eisenhüttenwesen*, **8**, 9–13 (1934).—Systems investigated include ferric oxide–ferrous oxide–silica alone, with calcium oxide, with alumina, and with calcium oxide and alumina. Degrees of oxidation were determined depending on the chemical composition at temperatures of 1230, 1320, and 1410°C. Calcium oxide increases the rate of formation of ferric oxide, and silica and alumina increase that of ferrous oxide. The ratio of calcium oxide over silica determines the type of oxides formed. Increasing the temperature increases the rate of dissociation of the components of the slag and the formation of ferrous oxide. The dissociation was found to be higher by 50% in the range from 1320 to 1410° than from 1230 to 1320°. One part (in weight) of calcium oxide may be replaced by 1.3 parts of ferrous oxide, and one part of silica by 1.4 parts of ferric oxide. W.M.C.

Primary X-ray method of chemical analysis. E. WAINER. *Jour. Amer. Chem. Soc.*, **56** [8], 1653–57 (1934).—A definite standardization of the variables of the spectrograph, photographic plate, analytical procedures, etc., must be adhered to rigidly to obtain comparable results of analytical worth. The use of log time-density was found to be a more suitable function for defining the plate characteristic for X-ray exposures than the usual log intensity-density. An absolute method of X-ray spectroscopic estimation from predetermined curves is suitable for analysis provided a filament which gives a uniform emission of electrons is used. Illustrated with curves.

F.G.H.

Plasticity, shrinkage, and other fundamental properties of clay in relation to the form of the clay particles. JULIUS ARON. *Notizblatt des Deut. Vereins für Fabrication von Ziegeln Tohnwaaren, Kalk, und Cement*, **9**, 167 (1873); translated by F. Salt in *Trans. Ceram. Soc.* [Eng.], **32** [11], 513–32 (1933).—A study is made of plasticity, shrinkage, and other properties of a number of clays of varying chemical composition. The shrinkage of a clay during drying takes place equally in all directions and is equal to the volume of the evaporated water; a fixed shrinkage limit, independent of the original water content of the clay, is reached before drying is complete when the wet clay particles being drawn closer together finally come into contact. The pore volume, calculated from the water remaining in the clay at the shrinkage limit as a percentage of the total volume, is approximately the same in the several clays and is close to the theoretical value of 35.1% voids for closely packed spherical particles. That the smallest of clay particles are spherical in form is shown by microscopic examination. Plasticity is explained on the basis of spherical particles arranged in a system having capillaries of uniform diameter.

R.H.H.P., JR.

Potassium sulfate from syngenite by high-temperature extraction with water. L. CLARKE AND E. P. PARTRIDGE. *Ind. Eng. Chem.*, **26** [8], 897–903 (1934).—In the recovery of potassium sulfate from polyhalite, conversion of the latter is made to syngenite, a double sulfate of potassium and calcium, and potassium sulfate is extracted from this substance. An improved method for decomposing syngenite is described which comprises a two-stage extraction with water at approximately 200°C. A process outline is suggested which will produce a concentrated solution of magnesium sulfate, a residue of solid calcium sulfate, and a technically pure potassium sulfate, with a recovery of 87% of the potassium sulfate initially present in the polyhalite. Illustrated. F.G.H.

Quantitative spectroscopic analysis of solutions. W. R. BRODE AND J. G. STEED. *Ind. Eng. Chem., Anal. Ed.*, **6** [3], 157–59 (1934).—Calibration curves have been determined for the quantitative spectrographic analysis of columbium, beryllium, titanium, vanadium, tungsten, iron, molybdenum, chromium, lead, and cobalt. These

curves are given in both per cent of element and logarithm of the per cent of element present. The average deviation in the determination of samples of known composition was less than 5% of the known concentration. Illustrated. F.G.H.

Rapid centrifugal estimation of small amounts of sodium. E. R. CALEY, C. T. BROWN, AND H. P. PRICE. *Ind. Eng. Chem., Anal. Ed.*, **6** [3], 202–205 (1934).—The sodium is precipitated as triple uranyl acetate, and the volume of the precipitate is measured in a special calibrated tube. The samples analyzed contained 0 to 0.1 mg. of sodium. F.G.H.

Recrystallization of disperse quartz. S. BRESSLER, E. STRAUFF, AND I. ZELMANOFF. *Physik. Z. Sowiet-Union*, **4** [5–6], 909–10 (1933); abstracted in *Physik. Ber.*, **15** [13], 1051–52 (1934).—While regular amorphous quartz recrystallizes at about 1000°C, recrystallization of disperse quartz takes place at about 400°C. The reason is ascribed to a specific surface phenomenon found in very thin films produced by the evaporation of quartz. M.H.

Separation and determination of the alkali metals, using perchloric acid. I. Solubilities of perchlorates of alkali metals in mixed organic solvents. G. F. SMITH. *Jour. Amer. Chem. Soc.*, **47** [3], 762–69 (1925). **II. Precise estimation of insoluble alkali metal perchlorates.** G. F. SMITH AND J. F. ROSS. *Ibid.*, pp. 774–81.—The correct drying temperature of the insoluble alkali perchlorates was found to be 350°C. **III. Normal butyl alcohol and ethyl acetate as mixed solvents in separation and determination of potassium, sodium, and lithium.** *Ibid.*, **47** [4], 1020–26 (1925).—The use of a mixture of equal parts of *n*-butyl alcohol and ethyl acetate is shown by test analyses to be satisfactory for (1) the extraction separation of potassium and sodium perchlorates, two extractions with intermediate solution of potassium perchlorate being required; (2) the extraction separation of potassium and lithium perchlorates, one extraction only being required; and (3) the separation of sodium and lithium subsequent to their extraction from potassium, following the procedure of Willard and Smith in which sodium chloride is precipitated from solution in *n*-butyl alcohol by a hydrogen chloride solution in the same solvent. **IV. Perchlorate-chloroplatinate method for determining potassium in the presence of sodium.** G. F. SMITH AND A. C. SHEAD. *Ibid.*, **54** [5], 1722–30 (1932).—Potassium and sodium in the form of their perchlorate solution in 50% ethyl alcohol and water mixture may be precipitated by the addition of an alcoholic solution of chloroplatinic acid and the potassium quantitatively separated in the form of potassium chloroplatinate. **V. Perchloric acid and chloroplatinic acid in determining small amounts of potassium in the presence of large amounts of sodium.** G. F. SMITH AND J. L. GRING. *Ibid.*, **55** [10], 3957–61 (1933).—The salts of sodium and potassium are converted to the neutral anhydrous perchlorates, dissolved in 95% alcohol, and treated with a moderate excess of chloroplatinic acid. F.G.H.

Spectrographic quantitative analysis; application for silicon. HENRI TRICHE. *Compt. rend.*, **199** [6], 419–21 (1934).—A method is described using spark or electric arc spectrum in connection with a solution of known composition in which the sample containing Si is dissolved. Wave-length 2881Å of Si is employed for the determination of Si; amounts of less than 0.5% can be detected. The method is particularly adapted for determining Si content in light metals. M.H.

System: PbO–SiO_2. R. F. GELLER, A. S. CREAMER, AND E. N. BUNTING. *Jour. Research Nat. Bur. Stand.*, **13** [2], 27–44 (1934); R. P. 705, price 5¢.—The system PbO–SiO_2, of interest to investigators and manufacturers of ceramic glazes and glasses, was investigated. It was found to contain the following three compounds, the optical properties, linear thermal expansions, and melting points of which were studied: $4PbO{\cdot}SiO_2$ occurring in 3 forms and melting incongruently at 725 ± 1°C; $2PbO{\cdot}SiO_2$, melting congruently at 743 ± 3°C; and $PbO{\cdot}SiO_2$, melting congruently at 764 ± 3°C. R.A.H.

System: Silica. F. FRANCESCHINI. *Ind. Silicati*, **11** [8], 5–12 (1933).—A résumé of data pertaining to the various modifications of silica and their interrelations is given. H.F.V.

Temperature-structure-composition behavior of certain crystals. M. J. BUERGER. *Proc. Nat. Acad. Sci.*, **20** [7], 444–53 (1934).—The structure and notation of polyatomic crystals are considered. The potential favoring the ordered modification, the favored state under thermal agitation, quenched crystals and variate atom equipoints, group rotation and extra specific heats, the possibility of solid solution, and unmixing or segregation from solid solution are discussed with the aid of algebraic notation and formulas. J.L.G.

Thermodynamics of solid solutions. I. Perfect solutions. H. SELTZ. *Jour. Amer. Chem. Soc.*, **56** [2], 307–11 (1934).—A graphical method is developed for determining the liquidus and solidus curves for binary systems which solidify with the formation of solid solutions from the fugacities or activities of the components in the two phases. Equations are derived for calculating the liquidus and solidus curves from the temperatures and heats of fusion of the two pure solids and the assumption that both solutions are perfect. F.G.H.

X-ray examination of ceramics. A. ZWETSCH. *Ber. deut. keram. Ges.*, **15** [1], 2–14 (1934).—Z. describes the Debye-Scherrer method of X-ray examination and gives his observations on the modification in structure of argillaceous matter, based on work with Zettlitz kaolin. Spectrographs of the kaolin are given on samples treated at various temperatures between 400 to 1000°C. Up to 450°C no modification is noticed, and only after a temperature of 550° is the initial spectra entirely modified. At this temperature the kaolinite is found in the amorphous state. Kaolinite (Al_2O_3–$2SiO_2$–$2H_2O$) and mica (K_2O-$3Al_2O_3$–$6SiO_2$–$2H_2O$) have the same Al_2O_3–SiO_2 ratio, which explains the similarity of the spectrograms. From 900°C the spectra again alter by the appearance of alumina and sillimanite lines. At 1000°C the alumina lines are the most apparent; at 1100°C only those of sillimanite appear. At about 1200°C a new crystalline substance is found, identified as cristobalite. At 1300°C cristobalite and sillimanite were present, but above this temperature no observations were made. E.J.V.

BOOKS

Conductivity Titrations and Conductivity Measurements.

Visual and Acoustic Methods with Examples for Use in Laboratories and Plants (Leitfähigkeitstitrationen und Leitfähigkeitsmessungen. Visuelle und akustistiche. Methoden mit Beispeilen für die Anwendung in Laboratorium und im Betrieb). G. JANDER AND O. PFUNDT Ferdinand Enke, Stuttgart, 1934, 88 pp. Reviewed in *Trans. Faraday Soc.*, **30** [7], 580 (1934).—Following a general introduction and the application of the Kohlrausch method to acid and alkali titration, modifications are described whereby the telephone may be replaced by a visible measuring instrument the detection of which may be used for following the course of a reaction. Different analytical applications and applications of the large scale are discussed. G.R.S.

Conductometric Analysis. H. T. S. BRITTON. Chapman and Hall, Ltd., London. 170 pp. Reviewed in *Trans. Faraday Soc.*, **30** [7], 579 (1934).—This monograph is a carefully compiled account of the present state of knowledge of conductometric analysis. The fundamental principles underlying the method are carefully explained and sufficient practical details are given to make it valuable as a laboratory textbook. Special attention has been directed to the titration of acids and bases and to estimations involving precipitation. G.R.S.

Treatise on the Catalytic Action of Surfaces. J. E. NYROP. Levin and Munksgaard, Copenhagen, 1934. 75 pp. Reviewed in *Chem. & Ind.*, **53** [29], 641–42 (1934). G.R.S.

General

Appeal of this Society to those who can not read the *Journal*. EDITORIAL. *Bull. Amer. Ceram. Soc.*, **13** [9], 217–18 (1934).

Chemical health hazards in industry. J. C. CUNNINGHAM. *Chem. & Ind.*, **53** [33], 707–10 (1934).—Silicosis is discussed; talc dust is similar in its effects. Within the last year it was suggested that sericite rather than SiO_2 was responsible for the condition brought about by talc. G.R.S.

Commercial development of kyanite in the South Atlantic states. V. L. MATTSON. *Bull. Amer. Ceram. Soc.*, **13** [9], 226–28 (1934).

Geographic roster of the American Ceramic Society. ANON. *Bull. Amer. Ceram. Soc.*, **13** [9], 234–54 (1934).

Mystical number "76." F. W. PRESTON. *Bull. Amer. Ceram. Soc.*, **13** [9], 228 (1934).

Objectivity in economics. R. E. FLANDERS. *Mech. Eng.*, **56** [2], 67–69 (1934).—F. discusses industry's requirements of engineering students in the way of economic training. F.G.H.

Practical results and prospects for clay de-airing. F. SLAVIK. *Tonind.-Ztg.*, **58** [37], 451–53 (1934).—Experiments are described showing that de-airing increases the tensile strength of the mass and its capability of molding. The properties of the fired bodies are improved, the drying time is shortened, and the firing is not affected. M.V.K.

Pronunciation of chemical words. E. J. CRANE. *Ind. Eng. Chem., News Ed.*, **12** [10], 202–205 (1934).—A list of 361 chemical words, with two or more possible pronunciations indicated for each, was sent by the nomenclature, spelling, and pronunciation committee of the American Chemical Society to four hundred chemists as representative of various interests in chemistry and of the various sections of the U. S. Accompanying the list was a questionnaire designed to bring out any special influences which may have affected each referee's pronunciation practice. The words studied and their pronunciations are listed alphabetically. F.G.H.

Researches on drying solid materials. V. Relationship between rate of drying and mixing proportions of quartz and feldspar with kaolin. SABURO KAMEI AND TAMOTSU SEDOHARA. *Jour. Soc. Chem. Ind.* [Japan], **37** [5], 288–92*B* (1934).—The duration of drying is shortened in reverse proportion to the amount of thinning agent. Tables and curves show the results. For Parts III–IV see *Ceram. Abs.*, **13** [7], 188 (1934). M.V.K.

Whom does the American Ceramic Society benefit? ROSS C. PURDY. *Bull. Amer. Ceram. Soc.*, **13** [9], 230–32 (1934).

BOOK REVIEWS

Imperial Institute Annual Report, 1933. WILLIAM FURSE. 55 pp. Price 2s. In presenting his final report, F. notes the growth of the Institute's activities from 1926 to 1933 which is indicated in the table on p. 13. Reorganization of the Exhibition Galleries resulted in a 100% increase in attendance, totaling over $4^1/_4$ millions in seven years. Materials tested in the ceramic laboratory of the Mineral Resources Department include kaolins from Burma, pottery clays from Ceylon, and clays from Nigeria which proved suitable for making earthenware, stoneware, and refractory brick. Total public attendance at the Galleries in 1933 was 738,718. Over 1800 schools use the Galleries and Cinema regularly for the study of Empire Geography. Many schools and colleges outside London give a whole day or series of days to the study of the exhibits of certain Dominions and Colonies. The coöperation of the Central Council for School Broadcasting of the B.B.C. has resulted in regular visits to the Galleries by many classes of scholars to listen to the broadcast talks on "Life and Work in the British Empire." Films seen by the scholars after each talk and the Gallery Exhibits inspected by them under the guidance of their teachers are said to contribute much to the value of these talks. The experiment is being closely watched by educational authorities in Great Britain.

Working of Raw Materials of the Ceramic Industry (Rohstoffbetriebe der keramischen Industrie). ALFRED LAUBENHEIMER. Theodor Steinkopff, Dresden, 1934. 150 pp., 56 illustrations. Unbound 10.00 Rm; bound 11.50 Rm. This book is the first volume of a collection of works edited by O. Krouse dealing with industrial ceramics. It reviews modern working and manufacturing methods used in the ceramic industry, including (1) determination of the deposits, (2) opening of the de-

posits, (3) determination of the value of a deposit, (4) working methods, (5) machines, (6) preparation of ceramic raw materials, and (7) control of operations. M.V.K.

BOOKS AND BULLETINS

A.S.T.M. Manual on Presentation of Data. ANON. American Society for Testing Materials, Philadelphia, Pa., 1934. 45 pp. Price 50¢. Reviewed in *Power*, **78** [3], 157 (1934). F.G.H.

Berl-Lunge Chemical-Technical Research Methods. Vol. V (Berl-Lunge chemisch-technische Untersuchungsmethoden). Edited by ERNST BERL. 8th ed. Julius Springer, Berlin, 1934. 1640 pp. Price 136 Rm. Reviewed in *Ind. Eng. Chem., News Ed.*, **12** [16], 307–308 (1934). For Vol. III see *Ceram. Abs.*, **12** [7], 281 (1933). F.G.H.

Comprehensive Treatise on Inorganic and Theoretical Chemistry. Vol. XIII. [Part II], Fe. J. W. MELLOR. Longmans, Green and Co., London and New York, 1934. 948 pp. Price $20.00. Reviewed in *Ind. Eng. Chem., News Ed.*, **12** [12], 237 (1934); *Jour. Amer. Chem. Soc.*, **56** [6], 1430 (1934). For Vol. XII see *Ceram. Abs.*, **12** [10–11], 403 (1933). F.G.H.

Crystal Chemistry of Inorganic Compounds (Kristallchemie der anorganischen Verbindungen). M. C. NEUBURGER. Ferdinand Enke, Stuttgart, 1933. 115 pp. Price 9.70 Rm. Reviewed in *Jour. Inst. Metals*, **53** [10], 605 (1933).—A section devoted to the structure of silicates is included in this volume. F.G.H.

Electric Furnaces. Improvement of the Character of Chemical Apparatus. Vol. I (Elektrische Ofen. Fortschritte des chemischen Apparatewesens). Edited by A. BRÄUER AND J. REITSTÖTTER. Akademische Verlagsgesellschaft m.b.H., Leipzig, 1934. 176 pp. Price 28 Rm. Reviewed in *Ind. Eng. Chem., News Ed.*, **12** [16], 309 (1934).—This volume is intended as a reference work on the patent literature of electric furnaces. F.G.H.

Electrokinetic Phenomena. H. A. ABRAMSON. Amer. Chem. Soc. Monograph Series, No. 66. Chemical Catalog Co., Inc., New York, 1934. 316 pp. Price $7.50. Reviewed in *Ind. Eng. Chem., News Ed.*, **12** [14], 267 (1934).—The electrokinetic behavior of clays, soils, and other inorganic materials is considered in this volume. F.G.H.

Elementary Engineering Thermodynamics. T. H. TAFT. John Wiley and Sons, Inc., New York, 1934. 229 pp. Price $2.75. Reviewed in *Power*, **78** [4], 211 (1934). F.G.H.

Fellowships and scholarships for advanced work in science and technology. Compiled by CALLIE HULL AND CLARENCE J. WEST. 3rd ed. *Bull. Nat. Research Council*, No. 94, 194 pp. (1934). Price $1.00. J.L.G.

Funds available in the United States for support and encouragement of research in science and its technologies. Compiled by CALLIE HULL AND CLARENCE J. WEST. 3rd ed. *Bull. Nat. Research Council*, No. 95, 162 pp. (1934). Price $1.00. J.L.G.

Inorganic Chemistry. Textbook for Advanced Study and Daily Use (Anorganische Chemie. Ein Lehrbuch zum Weiterstudium und zum Handgebrauch). F. EPHRAIM. 5th ed., revised and enlarged. Verlag von Theodor Steinkopff, Dresden-Blasewitz, Germany, 1934. 841 pp. Price 18 Rm. Reviewed in *Jour. Amer. Chem. Soc.*, **56** [8], 1826 (1934). For 2nd English ed. see *Ceram. Abs.*, **13** [9], 245 (1934). F.G.H.

Introduction to Modern Physics. 2d ed. F. K. RICHTMYER. McGraw-Hill Book Co., New York, 1934. 747 pp. Price $5.00. Reviewed in *Mech. Eng.*, **56** [6], 373 (1934). F.G.H.

Introduction to Theoretical Physics. J. C. SLATER AND N. H. FRANK. McGraw-Hill Book Co., New York, 1933. 576 pp. Price $5.00. Reviewed in *Mech. Eng.*, **56** [2], 125 (1934). F.G.H.

Kinetic Theory of Gases. 2d ed. L. B. LOEB. McGraw-Hill Book Co., Inc., New York, 1934. 687 pp. Price $6.00. Reviewed in *Jour. Amer. Chem. Soc.*, **56** [8], 1826 (1934). F.G.H.

Laboratory Manual of Colloid Chemistry. H. N. HOLMES. 3rd ed., rewritten and reset. John Wiley and Sons, Inc., New York, 1934. 229 pp. Price $3.25. Reviewed in *Jour. Amer. Chem. Soc.*, **56** [8], 1826 (1934). See also *Ceram. Abs.*, **13** [7], 195 (1934). F.G.H.

Luminescence Analysis in Filtered Ultra-Violet Light. Auxiliary Book in Working with the Analytical Lamp (Luminescenz-Analyse im filtrierten ultravioletten Licht. Ein Hilfsbuch beim Arbeiten mit den Analysen-lampen). 3rd revised ed. P. W. DANCKWORTT. Akademische Verlagsgesellschaft m.b.H., Leipzig, 1934. 190 pp. Price 8.50 Rm. Reviewed in *Jour. Amer. Chem. Soc.*, **56** [7], 1652 (1934). F.G.H.

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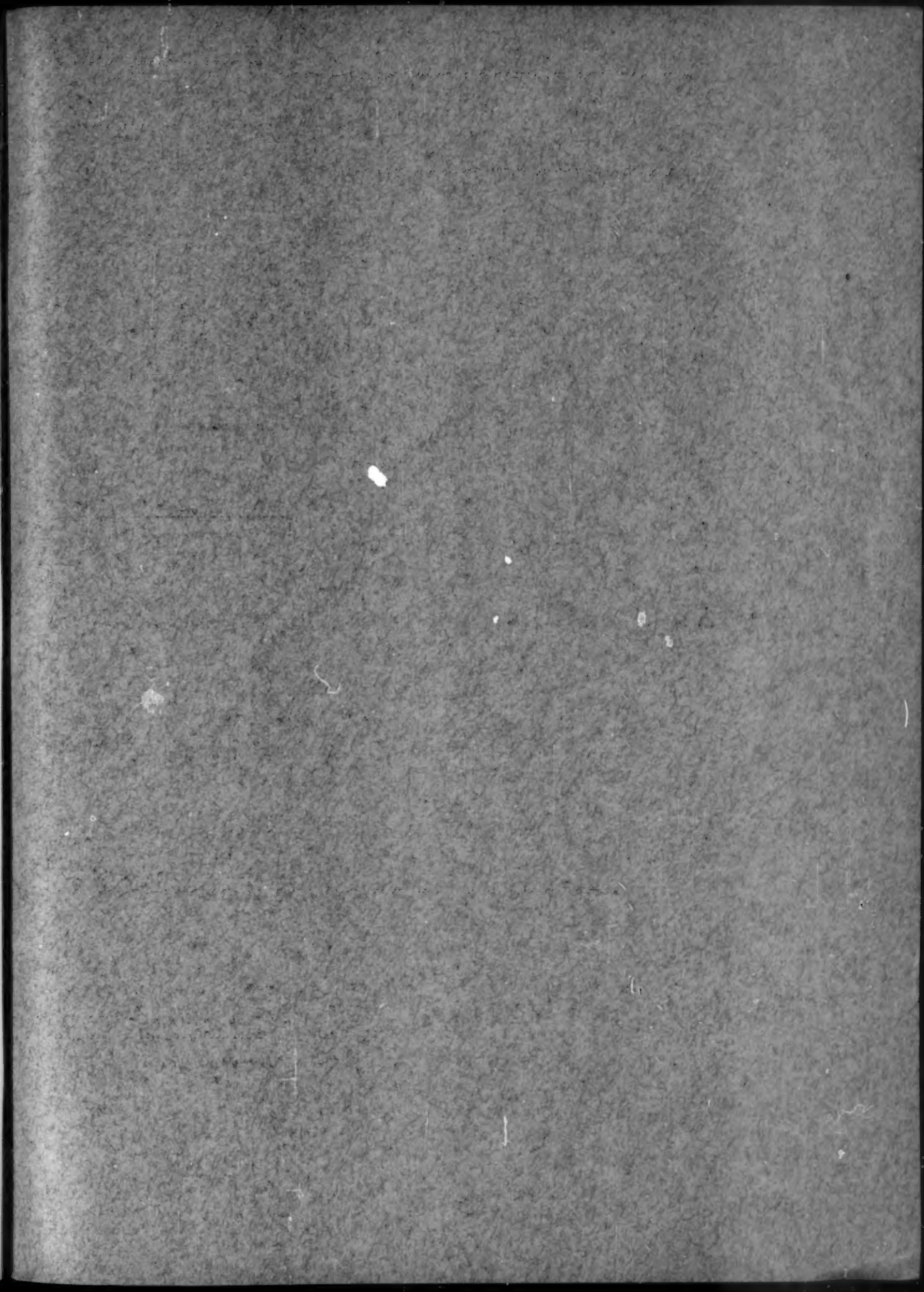
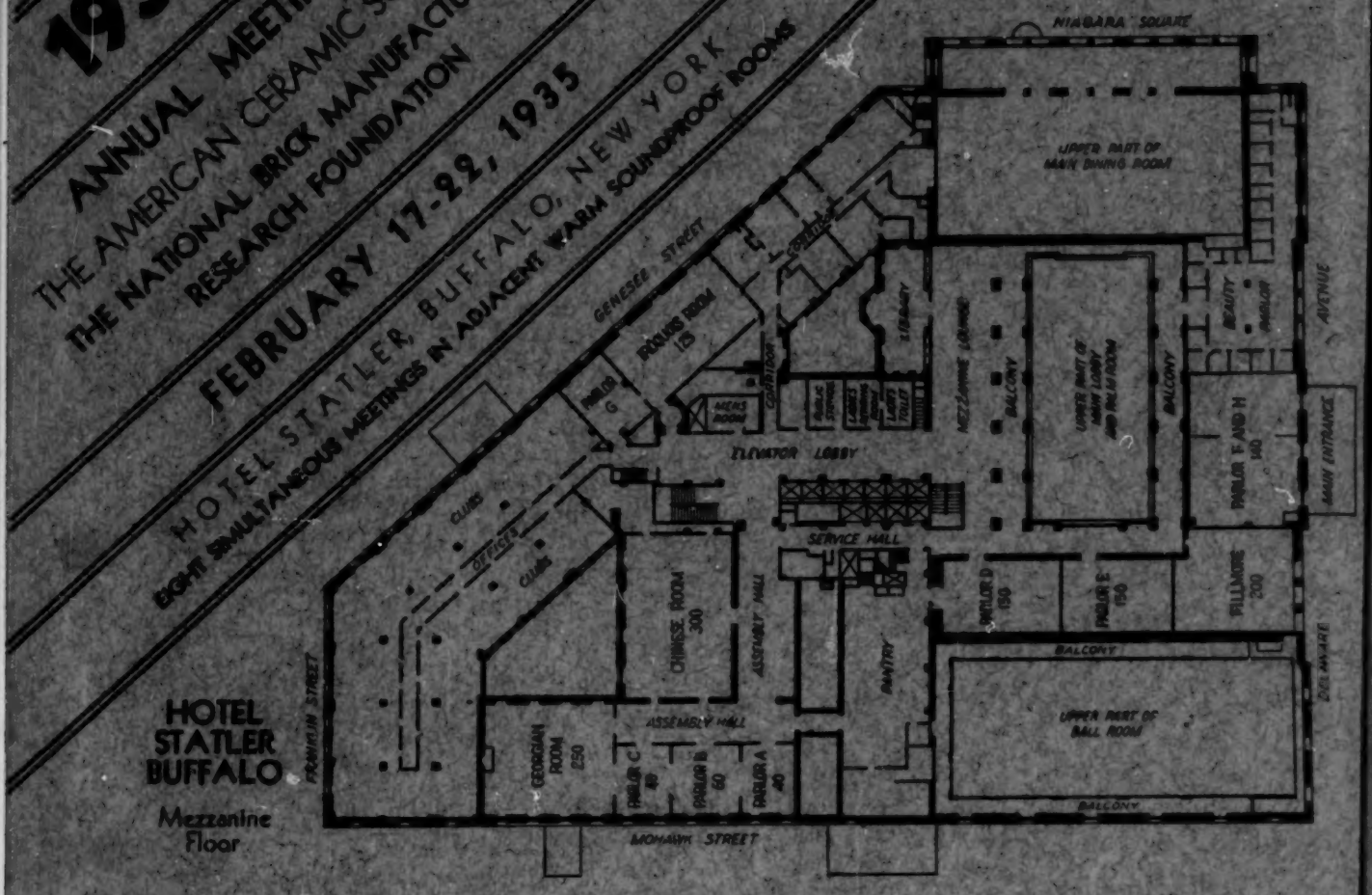


1935 ANNUAL MEETINGS

THE AMERICAN CERAMIC SOCIETY
THE NATIONAL BRICK MANUFACTURERS
RESEARCH FOUNDATION

FEBRUARY 17-22, 1935

HOTEL STATLER, BUFFALO, NEW YORK
EIGHT SIMULTANEOUS MEETINGS IN ADJACENT WARM SOUNDPROOF ROOMS



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